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PHYSICAL REVIEW

IMPACT FLUORESCENCE OF ZINC

By J. G. Winans

Abstract

Excitation of the zinc spectrum by collisions of the second kind with excited mercury atoms.—A sealed quartz tube containing zinc vapor at 16.0 mm and mercury vapor at 0.28 mm was illuminated by light of various wave-lengths from the hot and cold quartz mercury arcs and the aluminum spark. The resulting fluorescent radiation, observed with a short focus quartz spectrograph, contained several zinc lines which required more than 4.9 volts for their excitation. To account for these lines it is necessary to assume that mercury atoms in the 2^1P_1 and 2^3S_1 or 3^3D states are effective in impacts of the second kind. 2^1P_1 mercury atoms (energy 6.67 volts) were found to excite the first triplet of the sharp series of zinc requiring 6.62 volts but not the resonance line 3075 which requires 4.01 volts. This indicates that a collision between an excited mercury atom and a normal zinc atom is more likely to be one of the second kind if the energy of the excited mercury atom only slightly exceeds that needed to excite the zinc atom. A band, probably due to HgZn, formed in the excited state or excited by an impact of the second kind, was also observed in the fluorescent light.

I. Introduction

IT HAS been known for several years that a mixture of mercury and thallium vapors when illuminated by a water-cooled quartz mercury arc will emit a fluorescent radiation whose spectrum shows both mercury and thallium lines.[1,2,3,5,7] Similar effects have been observed for mixtures of mercury vapor with vapors of cadmium,[3] lead,[4] bismuth,[4] silver,[1] indium,[5] and sodium[3,6]. A summary of previous work has been given by Franck and Jordan.[8]

If we call those atoms mixed with the mercury vapor B atoms, the B radiation is assumed to result in the following manner. Mercury atoms reach an excited state through absorption of energy from the mercury arc, and transmit this energy to the B atoms through "impacts of the second kind." The B atoms later emit this energy as B radiation. If these excited

[1] G. Cario, Zeits. f. Physik **10**, 185 (1922).
[2] S. Loria, Phys. Rev. **26**, 573–85 (1925).
[3] G. Cario and J. Franck, Zeits. f. Physik **21**, 202 (1923).
[4] H. Kopfermann, Zeits. f. Physik **21**, 316 (1924).
[5] K. Donat, Zeits. f. Physik **29**, 345 (1924).
[6] F. Rasetti, Nature **118**, 47 (1926).
[7] J. Franck, Zeits. f. Physik **9**, 259 (1922).
[8] J. Franck, and P. Jordan, Anregung von Quantensprüngen durch Stösse, pp. 210–232.

mercury atoms have more energy than is needed to excite the B atoms, the energy left over is transformed into thermal kinetic energy of the colliding atoms. The corresponding increase in velocity of the B atoms causes them to emit their radiation with an abnormally large Döppler broadening. This increased Döppler broadening has been verified for the case in which the B atoms are sodium atoms, by F. Rasetti.[6] If the excited mercury atoms have not sufficient energy to excite the B atoms, the excited mercury atoms may, if the energy lacking is small, combine their energy with the thermal energy of the two colliding atoms and cause the excitation of the B atoms. This change of thermal energy to quantum energy has been assumed by Cario and Franck[3] to explain the fluorescence observed when the B atoms were cadmium atoms.

It has been observed that mixtures of argon, helium, or nitrogen, with the mercury and B atoms will increase the intensity of the B radiation.[2,5] In this case many of the excited mercury atoms in the 2^3P_1 state are assumed to be changed to the metastable 2^3P_0 state through impacts of the second kind with argon, helium, or nitrogen molecules. Mercury atoms in the metastable 2^3P_0 state are further assumed to endure many collisions with A, He, or N_2 molecules without losing their energy, and to transfer their energy upon collision with B atoms. This assumption is not unreasonable because the energy of the 2^3P_0 mercury atoms is very much less than that needed to excite the A, He, or N_2 molecules. As a result, the only way 2^3P_0 mercury atoms may return to normal is through impacts of the second kind with B atoms, exciting the B atoms ; or through impacts of the second kind with any other molecules, transferring all their energy into thermal energy. As will be shown later, the return through excitation of the B atoms is the more probable method.

The present work was undertaken to extend the observations to B atoms of zinc and to ascertain if possible, which excited mercury atoms transfer their energy to B atoms through impacts of the second kind.

2. The emission of radiation as a result of impacts of the second kind is important enough to deserve a good descriptive name. J. Franck[7] introduced the name "sensitized fluorescence" on account of the analogy with the sensitizing plates through staining. Loria[2] used the term "indirectly excited fluorescence," and F. Rasetti[6] called the phenomenon "activated fluorescence." None of these terms seems to give a satisfactory description of the process taking place, therefore the writer wishes to propose the name "impact fluorescence" which shall be defined as fluorescence excited through impacts of the second kind.

"Impact fluorescence" of zinc vapor was first observed by the writer in connection with the study of the fluorescence of zinc vapor excited by a zinc arc.[9] A preliminary report of the present work was given in Nature **118**, 46(1926).

[9] J. G. Winans, Nat. Acad. Sci. Proc. **11**, 742 (1925).

3. The notation used in this paper is that introduced by Russell and Saunders [10] with the serial numbers the same as those in Sommerfeld's notation.

Experimental Arrangement

4. The apparatus and method of preparing the tubes was very similar to that described by Loria,[2] the arrangement being shown in Fig. 1. All

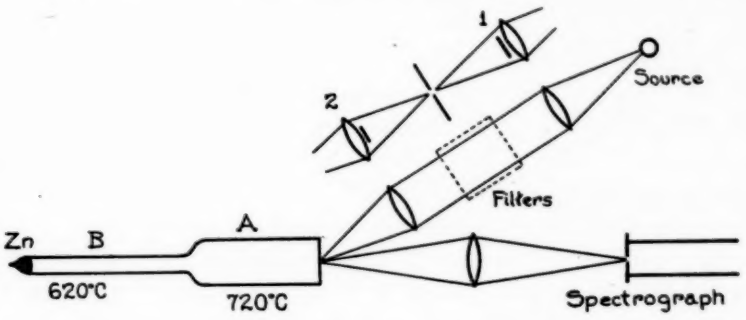

Fig. 1. Diagram of apparatus showing the arrangement for filtering the light. When desired, the lenses could also be arranged as shown at 1 and 2 with a system of diaphragms for the focal isolation of certain wave-lengths.

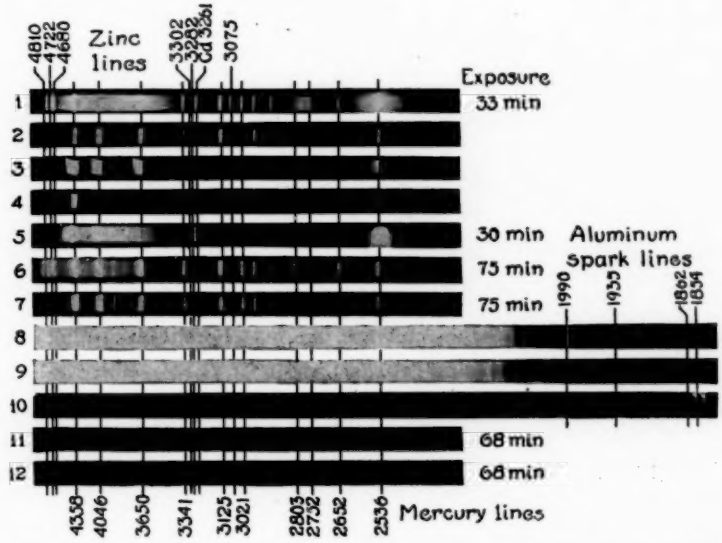

Fig. 2. (1) Impact fluorescence of zinc produced by the cooled Hg arc. (2) (3) Mercury arc (4) Mercury arc filtered through 17 cm of chlorine at atmospheric pressure. (5) Impact fluorescence produced by the cooled Hg arc through chlorine. (6) Impact fluorescence produced by a hot arc. (7) Impact fluorescence produced by a hot arc filtered through weak acetic acid. (8) Condensed aluminum spark. (9) Condensed aluminum spark filtered through thin glass. Thickness 5×10^{-4} mm. (10) Focal isolation of 1850–2000A from the condensed aluminum spark. (11) Impact fluorescence excited by 1850–2000A from the Al spark. (12) Impact fluorescence excited by 1950–2000A from the Al spark.

[10] H. N. Russell, and F. A. Saunders, Astrophys. J. **61**, 66 (1925).

optical parts were made of quartz. The tube contained a bead of zinc, and mercury vapor at 0.28 mm pressure. At the temperatures indicated, the zinc vapor pressure was 16.0 mm.* Eastman Speedway plates and Glycin developer were used.

The source of light was a Cooper Hewitt quartz mercury arc which could be run either hot or water-cooled. A horizontal magnetic field concentrated the discharge of the arc against the side nearest the fluorescent tube.

The quartz spectrograph contained a 60° prism 9x5 cm and lenses of diameter 7.0 cm, focal length 26 cm for 2536A.

5. In order to determine which mercury atoms are effective in the impact fluorescence of zinc, it is necessary to illuminate the zinc-mercury mixture by various combinations of wave-lengths from the mercury arc. The combinations used and the method of obtaining them are given in Table I. The transmissions of these light filters were obtained by photographing the quartz mercury arc or the aluminum spark through air, then through the filters, using the same exposure time. Two such sets are shown in Fig. 2. Nos. 3 and 4 show the transmission of chlorine vapor and Nos. 8 and 9 show the transmission of very thin glass. The absorption limit of the thin glass was called 1950A

TABLE I

Case	Wave-lengths in the exciting light.	Source	Filter
(a)	1849–7000A	Cooled mercury arc	Air. (Fig. 2, No. 2)
(b)	3200–7000	" " "	Glass lantern slide plate.
(c)	2300–7000	" " "	5 cm of weak acetic acid. Conc. 1–200.
(d)	2536 and 4358	" " "	17 cm of chlorine at atmospheric pressure. (Fig. 2, No. 4)
(e)	1849–7000 without 2536	Hot mercury arc.	Air
(f)	2300–7000 without 2536	" " "	5 cm of weak acetic acid.
(g)	1849–2000	Cooled mercury arc.	Focal isolation
		Hot mercury arc.	" "
		Condensed aluminum spark.	" " (Fig. 2, No. 10)
(h)	1950–2000	Cooled mercury arc.	Focal isolation and thin glass of thickness 5×10^{-4} mm.
		Hot mercury arc.	
		Condensed Al spark.	

Mercury atoms, at the pressures here used, have been shown to absorb only the core of the line at 2536A. This core is not in the light from the hot arc because of the reversal of 2536. The hot arc then effectively gives 1849–7000A without 2536. The 1849 line is also reversed in the hot arc, but from the results of this work, that does not prevent its absorption by normal mercury atoms. No effort was made to determine whether or not wave-lengths greater than 7000A were present. Their consideration has not thus far been necessary in the interpretation of the results.

* Landolt und Börnstein, Tabellen, 5th edition, 1923.

Impact Fluorescence of Zinc

6. *Case* (*a*). *Exciting light*, 1849–7000A. The spectrum of the fluorescent radiation is shown in Fig. 2, No. 1. No. 2 shows the mercury arc spectrum for comparison The zinc lines observed are given in Table II Enough cadmium was present to give the resonance line $1^1S_0-2^3P_1$. Two bands also appear in the fluorescent light. One is diffused toward the shorter wave-lengths from a head near 2770A and the other extends apparently continuously from 4800–3400A with a maximum near 3900A.

Table II

Wave-length	Notation	Intensity case (a)	Energy necessary to excite. (volts)	Remarks
4810	$2^3P_2-2^3S_1$	10		First member of the triplet
4722	$2^3P_1-2^3S_1$	10	6.62	sharp series.
4680	$2^3P_0-2^3S_1$	7		(sharp triplet).
3344?	$2^3P_2-3^3D$	3?		First member of the triplet
3302	$2^3P_1-3^3D$	2	7.74	diffuse series.
3282	$2^3P_0-3^3D$	1		(diffuse triplet)
3075	$1^1S_0-2^3P_1$	7	4.01	
2138	$1^1S_0-2^1P_1$	2	5.76	Resonance lines.
Cd 3261	$1^1S_0-2^3P_1$	10	3.78	

The line at 3344A was hidden by the mercury line at 3341A. Its intensity is predicted from the intensities of 3302 and 3282. The line at 2138A was obtained only with exposures of 30 minutes or more. The mercury lines in the exciting light always appear, from scattering at the fluorescent tube.

Case (*b*). *Exciting light*, 3200–7000A. No zinc lines appear. This shows that the zinc lines observed in case (a) are due to mercury wave-lengths less than 3200.

Case (*c*). *Exciting light*, 2300–7000A. All the lines of Table II were observed except 2138. The sharp triplet was very much reduced in intensity relative to the diffuse triplet and resonance line 3075. Most of the intensity of the sharp triplet must therefore be due to wave-lengths less than 2300. No conclusions can be drawn from the appearance or non-appearance of the resonance line 2138 on account of the insensitivity of the photographic plates in this region. The behavior of 2138 under various conditions could probably be determined by using plates covered with Nujol oil.

Case (*d*) *Exciting light*, 2536*A and* 4358*A*. *Fig.* 2, *No.* 5. The only zinc line which appears is 3075. The bands observed in case (a) and the cadmium line 3261 also appear. The cadmium line 3261 always appears with the zinc line 3075.

The zinc radiation observed is very probably due to 2536 alone. Absorption of 2536 excites mercury atoms to the 2^3P_1 state, and some of these may reach the metastable 2^3P_0 state through collisions of the second kind with normal zinc or mercury atoms. In the 2^3P_1 or 2^3P_0 state, the mercury atoms have sufficient energy to excite zinc atoms to the 2^3P_1 state, causing them to emit 3075 (see Fig. 3). 3075 is the only zinc line which 2536 has sufficient

energy to excite through the process just considered, and 3075 is the only zinc line observed.

Mercury atoms might absorb 2536 then 4358 giving them sufficient energy to excite the sharp triplet. No trace of the sharp triplet was observed with a 75 min. exposure, however, while a two minute exposure was sufficient to give the sharp triplet in case (a).

7. *Case (e). Exciting light,* 1849–7000A *without the core of* 2536. *Fig.* 2, *No.* 6. Only the sharp triplet of zinc appeared.

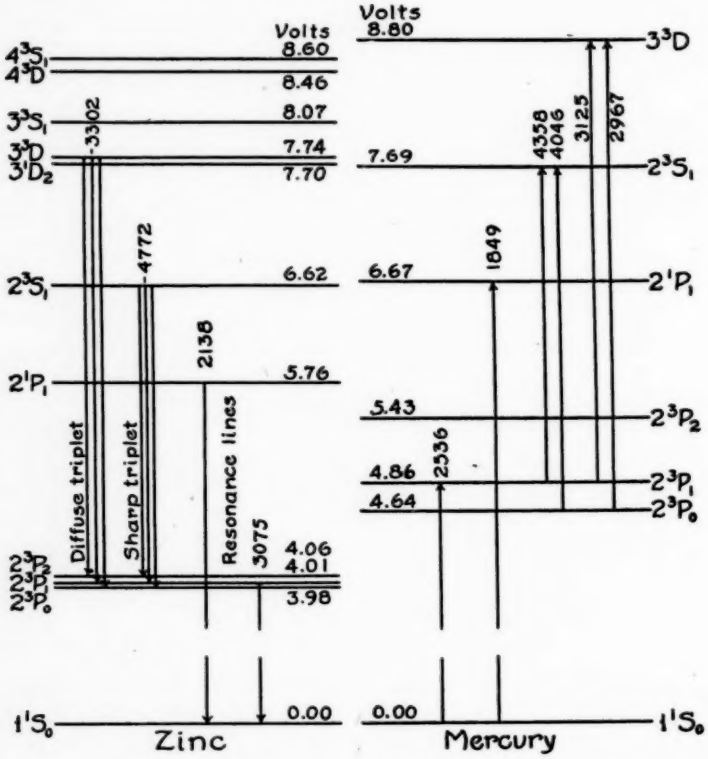

Fig. 3. Energy level diagrams of mercury and zinc.

Case (f). Exciting light, 2300–7000A *without the core of* 2536. *Fig.* 2, *No.* 7. No zinc lines appear. Cases (e) and (f) show that the zinc sharp triplet can be excited by wave-lengths between 1849 and 2300A. This was also indicated in case (c). In order to determine more accurately the effective range of wave-lengths, the focal isolation arrangement was used.

Case (g). Exciting light, 1849–2000A *from the cooled mercury arc, the hot mercury arc, and the condensed aluminum spark. Fig.* 2, *No.* 11. In each of these cases the zinc sharp triplet appeared. The intensity was greatest when the condensed aluminum spark was used as the source and least when the source was the cooled mercury arc. If now all wave-lengths less than 1950A are absorbed by a very thin piece of glass, the sharp triplet disappears.

Case (h). Exciting light, 1950–2000A. *Fig.* 2, *No.* 12. No zinc lines appear. A slight amount of scattered light of wave-length greater than 2000A and a band due to light from the furnace are observed in cases (g) and (h).

8. We have thus shown that the zinc sharp triplet can be excited by radiation between 1849 and 1950A. From Fig. 3 we see that 6.62 volts are required to raise a zinc atom from 1^1S_0 to 2^3S_1 so that it may emit the sharp triplet $2^3P_{2,1,0}-2^3S_1$. The exciting radiation must then possess at least 6.62 volts energy corresponding to a maximum wave-length of 1870A.

We can now trace the process of excitation from Fig. 3. Normal mercury atoms absorb 1849 from the mercury arc or 1854 and 1862 from the aluminum spark, thereby reaching the 2^1P_1 state. While in this state they undergo impacts of the second kind with normal zinc atoms leaving the zinc atoms in the 2^3S_1 state. These zinc atoms emit the sharp triplet.

The ability of the normal mercury atoms to absorb 1854 and 1862 from the aluminum spark is due to the broad absorption band of mercury which extends from 1849 toward the longer wave-lengths, becoming broader with increased pressure.[11]

9. We have yet to account for the zinc diffuse triplet and that part of the sharp triplet which remained when all wave-lengths less than 2300A were filtered out of the exciting light from the water cooled mercury arc. In order that a zinc atom may emit the diffuse triplet, it must be raised to the 3^3D state, which represents an energy of 7.74 volts. This is more than that possessed by a 2^1P_1 mercury atom and it can be observed under conditions such that no 2^1P_1 mercury atoms are present (case (c)). It must then be due to impacts of the second kind with mercury atoms in excited states of energy nearly equal to, or greater than 7.74 volts. From Fig. 3 we see that the lowest excited states of mercury with the required energy are 2^3S_1 representing 7.69 volts, and 3^3D representing 8.80 volts. Considering, for example, the 3^3D state, we see from Fig. 3 that to reach this state, mercury atoms must first absorb 2536 and then 3125 or 2967 depending on whether they are in the 2^3P_1 or 2^3P_0 state. These 3^3D mercury atoms may transfer their energy to normal zinc atoms through impacts of the second kind, leaving the zinc atoms in the 3^3D state.

This process requires 2536 and 3125 or 2967 in the exciting light, and if either 2536 or 3125 and 2967 are removed, the diffuse triplet should not appear. This is actually what is observed. 2536 is removed and 3125 and 2967 are transmitted when the hot arc through acetic acid is used as a source (case (f)). 3125 and 2967 are removed and 2536 transmitted when the cooled arc filtered through chlorine, served as the source (case (d)). In neither case was the diffuse triplet observed.

While it can be definitely stated that the absorption by mercury atoms of 2536 and 4358 is only slightly, if at all, effective in exciting the zinc diffuse triplet, it is possible that the combination of 2536 and 4046 absorption may be as effective as the combination of 2536 plus 2967 or 3125, since the chlorine filter which cuts out these two lines also cuts out 4046. The change in in-

[11] J. S. Van der Lingen and R. W. Wood, Astrophys. J. **54**, 155 (1921).

tensity of the diffuse triplet produced by inserting the chlorine filter is due to the elimination of the 3^3D state plus the elimination of the 2^3S_1 state as reached through the metastable 2^3P_0 state. The 2^3S_1 state can of course only be effective in exciting the zinc diffuse triplet if it combines its energy with 0.05 volts of thermal energy.

The appearance of the zinc sharp triplet when the exciting light did not contain 1849, is also explained by assuming double absorption in the mercury atoms and collisions of the second kind with normal zinc atoms. The possibility of exciting atoms in this way was discussed by Franck and Jordan.[12]

10. An alternative explanation for the appearance of the zinc diffuse triplet is that 2^3P_1 or 2^3P_0 mercury atoms combined their energy with thermal energy to excite the zinc atoms. This would mean that 2.88 volts were received from thermal energy. The probability that an atom at 720°C will have this much energy is less than 2.0×10^{-7}, making this explanation out of the question. Another possibility is a double process in the zinc atoms, normal zinc atoms being excited to 2^3P_2, 2^3P_1, or 2^3P_0 through impacts of the second kind with 2^3P_1 or 2^3P_0 mercury atoms and then being carried to 2^3S_1 or 3^3D through additional impacts with other 2^3P_1 or 2^3P_0 mercury atoms. Either of these alternative processes could occur if the exciting light contained λ2536 alone. The zinc sharp and diffuse triplets, however, were not observed with an exposure of 75 minutes in case (d) where the exciting light contained λ2536 and λ4358. In case (a) the diffuse triplet could be obtained with 5 minutes exposure.

We can conclude that the zinc sharp and diffuse triplets observed in case (c) were produced by impacts of the second kind with mercury atoms in the 3^3D or 2^3S_1 states.

11. The process involved in the production of the zinc diffuse triplet could be further studied by illuminating the fluorescent tube from two mercury arcs ; one, filtered through chlorine, to excite mercury atoms to the 2^3P_1 state, and the other, filtered through $HgCl_2$ (conc. 1–4) to raise the 2^3P_1 or 2^3P_0 mercury atoms to 2^3S_1 or 3^3D. $HgCl_2$ will absorb all wave-lengths less than 2700. This has been tried but so far without any positive results on account of experimental difficulties.

Probability of an Impact of the Second Kind

12. It has been observed[13] that an impact of the second kind was more likely to occur when the energy available nearly equals that needed to produce the observed phenomena. The energy values of the excited states of zinc and mercury make possible a further test of this statement. Referring to Fig. 3, we see that the 2^1P_1 state of mercury corresponds to an energy of 6.67 volts ; the 2^3S_1 state of zinc to an energy of 6.62 volts ; and the 2^3P_1 state of zinc to 4.01 volts. If it is true that impacts of the second kind are more probable when the energy available nearly equals that needed, 2^1P_1 mercury atoms should excite 2^3S_1 zinc atoms more than 2^3P_1 zinc atoms. This

[12] Franck and Jordan, loc. cit., p. 231.

[13] Franck and Jordan, loc. cit., p. 226.

would cause the sharp triplet ($2^3P_{2,1,0}-2^3S$) to be stronger in the fluorescent light than the resonance line ($1^1S_0-2^3P_1$) in all cases where the 2^1P_1 mercury atoms alone are effective. This, in fact, was observed. 2^1P_1 mercury atoms are the only excited mercury atoms directly produced when the exciting light contains only wave-lengths near 1849A. In all of these cases ((e), (g)) the sharp triplet appeared and the resonance line ($1^1S_0-2^3P_1$), λ3075, did not appear with exposures of 60–75 minutes. In case (a) the resonance line is strong with an exposure of only five minutes.

13. An objection to comparing the intensities of the sharp triplet and the resonance line 3075 is that the resonance line might be absorbed by the normal zinc vapor, making its intensity less, if it was emitted, than the sharp triplet which cannot be absorbed by the normal zinc vapor. If 2^3P_1 zinc atoms were produced by impacts of the second kind with 2^1P_1 mercury atoms, these excited zinc atoms would have an abnormally high velocity due to the change of the extra 2.66 volts into thermal energy. This would result in the resonance line being emitted with such a large Döppler shift that it would be rendered nearly un-absorbable by the normal zinc vapor. The non-appearance of the resonance line in impact fluorescence produced by 2^1P_1 mercury atoms therefore indicates that impacts of the second kind are more probable when the energy available only slightly exceeds that needed.

14. Referring again to Fig. 4 : if impacts of the second kind are more probable when the energy available nearly equals that needed, we should expect to have a very great accumulation of zinc atoms in the 3^1D_2 state whose energy of 7.70 volts nearly coincides with the energy of 7.69 volts of the 2^3S_1 state of mercury. These zinc atoms would emit 6362 ($2^1P_1-3^1D_2$) which is not observable in this experiment, being hidden by the continuous light from the furnace. This line, however, was observed by Lord Rayleigh[14] in the radiation emitted when a stream of excited mercury atoms met a stream of normal zinc atoms. It is not possible to say definitely from Lord Rayleigh's work which excited mercury atoms served to produce particular excited states of zinc atoms. The results, however, are in good agreement with the assumption that 2^3P_1, 2^3P_0, 2^1P_1, 2^3S_1, and 3^3D states of mercury may take part in impacts of the second kind.

15. Duffendack and Compton[15] have observed a relation between the probability of dissociation of hydrogen through impacts of the second kind, and the degree of coincidence between the energy available and that needed in the dissociation process. The quartz fluorescent tubes used in the present work gradually lose their vacuum with continued heating at about 700°C. It was observed that as gas leaks into the tube, the zinc lines due to the 2^3P_1 and 2^3P_0 states of mercury very soon disappear while the sharp triplet, largely due to 2^1P_1 mercury atoms, may still be excited with only a slight decrease in intensity. This indicates that the 2^1P_1 mercury atoms have more endurance when colliding with these gas molecules than the 2^3P_1 or 2^3P_0

[14] Lord Rayleigh, Proc. Roy. Soc. London **112**, 14–30 (1926).
[15] O. S. Duffendack and K. T. Compton, Phys. Rev. **23**, 588 (1924).

mercury atoms. The penetrating gas is probably hydrogen whose energy of dissociation is about 4.3 volts.[16] The greater endurance of the 2^1P_1 mercury atoms can be explained on the hypothesis that dissociation through impacts of the second kind is less probable when the energy available greatly exceeds that needed.

Bands Observed in the Fluorescent Radiation

16. In cases (a) and (d) two bands were observed in the fluorescent radiation. Both these bands are due to exciting light of wave-length near 2536A. The one with a maximum at λ3900 is probably due to mercury hydride. Mercury hydride bands have been studied by Hulthèn.[17]

17. The band at 2770A gives some evidence of fine structure. Its intensity increases and decreases with the vapor pressure of the zinc and does not depend on distillation of vapor from the zinc metal. It requires the presence of both mercury and zinc in the fluorescent tube for it was not observed, with like exposures, in a tube containing mercury alone, illuminated by a mercury arc, or in a tube containing zinc alone, illuminated by either a zinc or mercury arc. A possible explanation would be that an excited mercury atom combined with a normal zinc atom to form an excited HgZn molecule which emitted this band and then dissociated. For a given supply of excited mercury atoms per second, the band intensity should vary with the pressure of the zinc, and this indeed, was observed. This band might also be due to an excited zinc-normal-mercury molecule or to a normal HgZn molecule excited through impacts of the second kind.

In conclusion, I wish to express my sincere thanks to Drs. C. E. Mendenhall and R. C. Williamson under whose direction this work was carried out and whose ready advice is greatly appreciated. I wish also to thank Mr. H. R. Lillie for making Schumann plates to fit the spectrograph.

Physics Department,
University of Wisconsin,
March 25, 1927.

[16] E. E. Witmer, Phys. Rev. **28**, 1223 (1926).
[17] Hulthèn, Zeits. f. Physik **32**, 32 (1925).

DISSOCIATION OF HYDROGEN BY ELECTRONS

By A. Ll. Hughes and A. M. Skellett

Abstract

Variation with pressure of the rate of dissociation of hydrogen by electron impact.—Electrons were driven down the axis of a tube containing hydrogen. Atomic hydrogen formed by dissociation was condensed on the walls of the tube which was immersed in liquid air. The rate of dissociation was calculated from the rate of change in pressure as measured by a special hot wire gauge which was so designed that the galvanometer deflection was strictly proportional to the pressure from less than 10^{-5} mm to 0.27 mm. The deflections were recorded photographically. With both 100 volt electrons and 20 volt electrons the rate of diminution of pressure is directly proportional to the pressure. Hence the dissociation of hydrogen by electron impact cannot be a secondary effect, the result of a collision between a neutral hydrogen molecule and an ionized or excited molecule, unless the mean free path of the ionized or excited molecule is less than 1/300 that of the normal molecule. This latter is a most unlikely possibility. The dissociation is therefore very probably produced as a direct result of the impact of an electron on the molecule, a result which is strongly supported by the studies of intensities of hydrogen lines at different pressures by Blackett and Frank, and by Lowe.

Electron energy necessary to dissociate hydrogen.—It was found that dissociation began when the electrons had an energy corresponding to 11.5 volts.

IN A previous research[1] one of the authors investigated the dissociation produced in hydrogen by electronic bombardment. It was emphasized later[2] that this investigation pointed to the result, that the dissociation of the hydrogen molecule must be the direct result of an electron inpact. However Dempster,[3] Smyth,[4] and Hogness and Lunn[5] have shown by their positive rays analysis of the products of ionization that, when a collision between an electron and a molecule of hydrogen results in ionization, the direct result is undoubtedly a molecular ion. An atomic ion does not occur as the direct result of the impact of an electron on the molecule. It occurs only as the result of a secondary process such as a collision between a positively charged molecule and a neutral molecule. It was therefore thought desirable to re-examine the nature of the dissociation appearing when electrons are driven through hydrogen. The principle of the method is to measure the amount of dissociation, as indicated by the diminution of pressure in hydrogen from different initial pressures, when a constant electron current passes through it. If the dissociation is a direct result of the impact of an electron on a molecule, then the amount of dissociation should be proportional to the number of collisions between electrons and molecules, i.e., proportional

[1] A. Ll. Hughes, Phil. Mag. **41**, 778 (1921).
[2] A. Ll. Hughes, Phil. Mag. **48**, 56 (1924).
[3] A. J. Dempster, Phil. Mag. **31**, 438 (1916).
[4] H. D. Smith, Phys. Rev. **25**, 452 (1925).
[5] T. R. Hogness and E. G. Lunn, Phys. Rev. **26**, 44 (1925).

to the pressure. If, on the other hand, the dissociation is due to the collisions between molecular ions and neutral molecules, since the number of molecular ions formed, and the number of collisions between them and neutral molecules, are each separately proportional to the pressure, then the amount dissociated should be proportional to the square of the pressure. These considerations of course hold only when the mean free paths of the electrons and molecular ions are decidedly longer than certain dimensions of the apparatus. In view of Smyth's inference[4] that the mean free path of the hydrogen molecular ion is fifteen times less than that of a neutral molecule, it is necessary to extend the investigation in the direction of lower pressures.

Apparatus and Method

The apparatus is shown in Fig. 1. The tube D, in which the dissociation takes place, is about 30 cm long and 2 cm in diameter. An oxide coated filament F supplies the electron current. The electrons are accelerated to the grid G by a suitable potential difference. The part of the dissociation tube D below the grid is lined with a conducting film C of evaporated tungsten, which is insulated from the grid G, and from the "end plate" E at the bottom of the tube. When the leads (not shown) to G, C and E are connected together, the electrons travel with constant speed from the grid

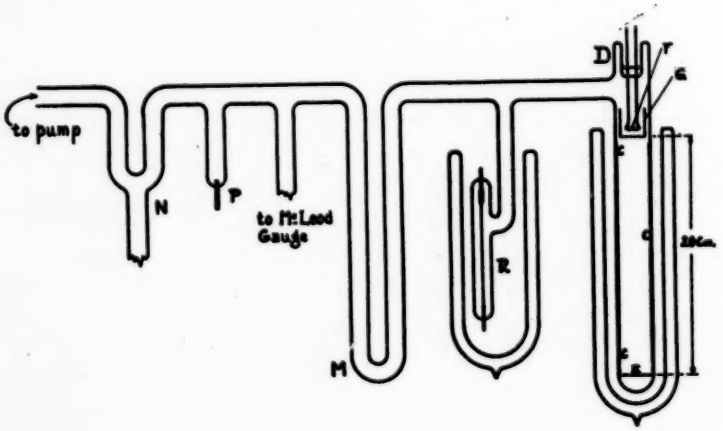

Fig. 1. Diagram of apparatus.

G to the end plate E. A magnetic field of 320 gauss, co-axial with the dissociation tube is sufficient to keep practically all the electrons travelling down the center of the tube (the number going to the tungsten coating C being less than 0.1 percent of the number travelling all the way to E). During an experiment the tube D is surrounded by liquid air to condense the hydrogen atoms as they impinge on the walls. This experimental arrangement is very satisfactory in that the electrons are compelled to travel along the tube, thus giving them the opportunity to make the maximum number of collisions possible, while the region along which the impacts occur is never more than 1 cm from the walls thus affording the products

of the impacts an opportunity of reaching the walls with a minimum chance of colliding with neutral molecules on their way.

To measure the decreasing gas pressure as the dissociation proceeded, a simple form of hot wire gauge was devised. It consisted of a 1 mil tungsten wire R, 5 cm long, mounted along the axis of a tube 8 mm in diameter. A two cell storage battery sent a current through the tungsten wire in series with an approximately equal resistance R' (Fig. 2). With the highest attainable vacuum in the gauge, the potential fall along R was balanced against a single cell storage battery E_2, by adjusting the shunt X across R', using the galvanometer G as an indicator. On admitting hydrogen, the galvanometer showed a deflection, increasing with the amount of hydrogen present. A careful calibration showed that the deflection of the galvanometer was very accurately proportional to the pressure from the lowest measured (0.000008 mm) up to 0.27 mm. A suitable shunt across the galvanometer

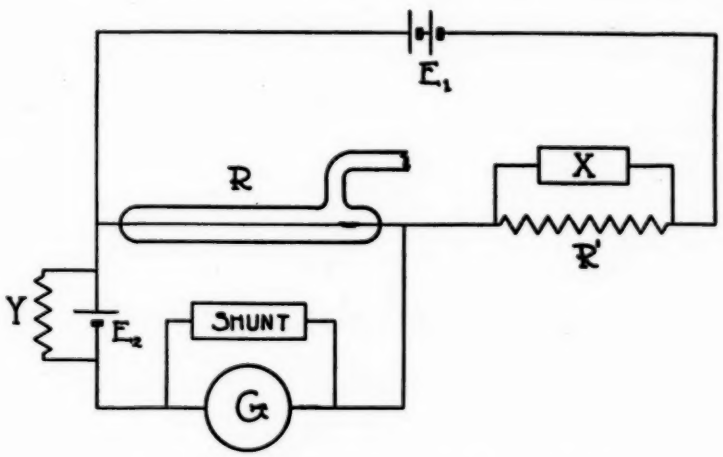

Fig. 2. Hot wire vacuum gauge and connections.

enabled us to get accurate readings at any selected part of the extended range of pressures which called for investigation. The lowest pressure measurable seemed to be determined principally by the constancy of the batteries. It was found that a resistance Y across E_2, chosen so that the e.m.f. of E_2 decreased at the same rate as that of E_1 added materially to the steadiness of the galvanometer zero when extremely low pressures were being investigated. The hot wire gauge itself was immersed in a Dewar flask containing distilled water at room temperature, since constancy of temperature of the gauge is vital to steadiness of the zero. A novel feature of the investigation was the photographic recording of the pressure change as indicated by the galvanometer deflection. A sample record is shown in Fig. 3. The vertical lines indicate one minute intervals, recorded automatically. Up to A we have (part of) the record with no gas in the tube but with the electron current flowing. This shows no evolution of gas due to electronic bombardment. At A the electron current was stopped and

hydrogen was admitted. (The admission of too much hydrogen at the beginning, and its correction, accounts for the initial irregularity.) The galvanometer record is again perfectly steady. Then at B the electron current of 8 microamps. was turned on and the pressure dropped approximately exponentially. At the end of 9 minutes, the gas was pumped out and the rest of the record (the latter part of which is cut off) shows the zero line again.

After a prolonged initial outgassing at the beginning of a set of experiments, the same procedure was always followed before each dissociation run. The apparatus to the right of the mercury trap was outgassed by heating to about 300°C for thirty minutes, with the condensation pump in operation. Then after isolating the apparatus from the pumps by means of the mercury cut off N, a definite amount of hydrogen was admitted through the palladium tube P. The electron current, measured to $C+E$ (though C took an inappreciable fraction), accelerated by the voltage desired, was held constant

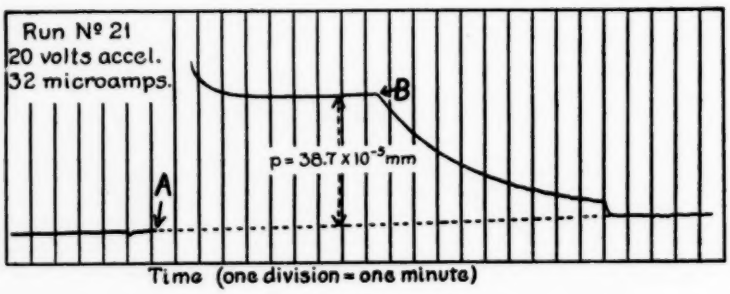

Fig. 3. Sample of photographic record of pressure changes.

at the pre-arranged amount, by slight adjustment, when necessary, of the filament heating current. Meanwhile the pressure decrease was being recorded by the galvanometer connected to the hot wire gauge H. A dissociation run lasted eight or nine minutes. Control experiments to test the behaviour of the gauge, (1) when hydrogen was in the apparatus but with no electron current flowing, and (2) when an electron current was flowing, but with no hydrogen in, were always made just before the dissociation experiment. After each such run, the liquid air around D was removed and the tube outgassed for the specified time to drive off all the condensed hydrogen atoms. It was then ready to start another dissociation run.

Results

Let d be the path traversed by the electrons (approximately the length of the tube) and λ be the mean free path. Let δn_0 electrons pass down the tube in a time δt, so that $\delta n_0 = i\delta t$ where i is the electron current. The number colliding with molecules on the way is

$$\delta n_0(1-e^{-d/\lambda}) \qquad (1)$$

Let these collisions result in the dissociation of δm molecules, the atoms formed being condensed and thereby resulting in a diminution of pressure $\delta p = \delta m/\alpha$. Let b be the ratio of the number of molecules dissociated to the number of collisions,—b is therefore a sort of efficiency of dissociation factor.

$$b = \frac{\delta m}{\delta n_0(1-e^{-d/\lambda})} = \frac{\alpha \delta p}{i\delta t(1-e^{-pd/\beta})} \tag{2}$$

since $\lambda = \beta/p$. If the pressure p is sufficiently low, the equation becomes

$$b = \frac{\text{const.}}{i}\ \frac{1}{p}\ \frac{dp}{dt} = \frac{\text{const.}}{i}\ \frac{d(\log p)}{dt}.$$

Since b is a collision constant, it is independent of the pressure, and we have, when i is constant

$$d(\log p)/dt = \text{const.} = b_1. \tag{3}$$

Thus, if the process of dissociation in this investigation is as pictured here, the derivative of log p with respect to the time should be constant (always provided that the pressure is sufficiently low). If however the impact of the electron on the molecule does not dissociate the molecule, but merely ionizes it, or excites it, and if dissociation now results from a collision between this molecule and a neutral one, we get a different expression. From (1), the number of excited or ionized molecules produced will be

$$\gamma \delta n_0(1-e^{-d/\lambda})$$

where γ is a constant. The number of collisions which these molecules make while on their path d_1 to the walls, with neutral molecules, is

$$\gamma \delta n_0(1-e^{-d/\lambda})(1-e^{-d_1/\lambda_1})$$

where λ_1 is the mean free path of the excited or ionized molecules. Let the fraction b' of these collisions result in the dissociation of δm molecules leading as before to a diminution of pressure $\delta p = \delta m/\alpha$. As before,

$$b' = \frac{\delta m}{i\,\delta t\,\gamma(1-e^{-d/\lambda})(1-e^{-d_1/\lambda_1})} \tag{4}$$

Putting $\lambda = \beta p$ and $\lambda_1 = \beta_1 p$, we have

$$b' = \frac{\alpha \delta p}{i\,\delta t\,\gamma(1-e^{-pd/\beta})(1-e^{-pd_1/\beta_1})} \tag{5}$$

If the pressure is sufficiently low, we may make the same approximations as before and get

$$b' = \frac{\text{const.}}{i}\ \frac{1}{p^2}\ \frac{dp}{dt} = \frac{\text{const.}}{i}\ \frac{1}{p}\ \frac{d(\log p)}{dt}$$

Since b', like b, is a collision constant, it is independent of the pressure, and we have

$$d(\log p)/dt = p \times \text{const.} = b_1' p \tag{6}$$

If this picture of the mechanism of dissociation be the correct one, then, at sufficiently low pressures, the derivative of log p should be proportional to the pressure.

In view of the foregoing considerations, each experimental curve (of which Fig. 3 is an example) in which the pressure is recorded photographically as a function of the time, was measured up and re-plotted as log p against the time. Two such curves are shown in Fig. 4. In the first one, the initial pressure was 39.6×10^{-5} mm, while in the latter it was 13.3×10^{-5} mm. It will be noticed that the first one is concave upwards. At first sight one might infer

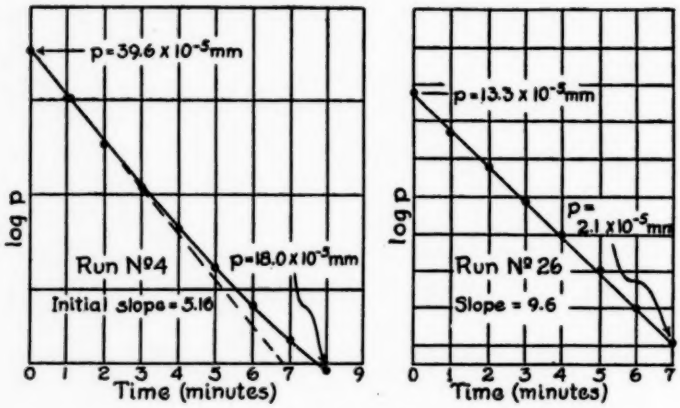

Fig. 4. Curves showing the variation of log p with time.

that this was a situation between the extreme cases corresponding to equations (3) and (6) respectively. The true explanation, however is given in Langmuir's early work on thermal dissociation of hydrogen. When an appreciable fraction of the cooled surface has been covered with condensed atoms, an atom subsequently produced by the dissociation process may hit a spot already occupied by an atom, in which case the two atoms come back again into the gas as a molecule and so no diminution in pressure is recorded. In this way, it is readily seen that as the surface becomes more and more occupied, the amount of dissociation per collision (the slope of the curve) apparently gets less, as shown by the curvature of the log p curve. In the experiments at the lowest pressures, however, so little of the surface is occupied by atoms, even at the end of a run, that the rate of diminution of pressure accurately reflects the dissociation per collision at all stages. To compare the real rates of dissociation per collision for different initial pressures, it is therefore necessary to compare the *initial* slopes of the various log p curves, since the beginning of each curve corresponds to a cold surface free of any atoms and therefore able to hold all those impinging on it.

The pressures in the dissociation tube, at the temperature of liquid air, are lower than those in the gauge in accordance with the rule governing the equilibrium of gases at low pressures in a system in which the temperature is different at different places. Thus if the temperatures in the gauge and dissociation tube are respectively T_G and T_D, the corresponding pressures are given by

$$P_G/P_D=(T_G/T_D)^{1/2}=(293/90)^{1/2}=1.80$$

This factor is used in evaluating the pressure in the dissociation tube from the indications of the gauge.

The results of several runs, each beginning with a different initial pressure are collected in Table I and Table II.

TABLE I

Electron energy = 100 volts: Electron current = 8 microamperes.

Number of run	Initial pressure	Initial slope of log p curve
3	286×10^{-6} mm	4.15
1	48	4.15
4	39.6	5.16
5	27.4	5.8
8	12.4	5.7
6	10.4	6.0

Pressure at end of run No. 6 = 3.6×10^{-6} mm.

TABLE II

Electron energy = 20 volts: Electron current = 32 microamperes.

Number of run	Initial pressure	Initial slope of log p curve
9	405×10^{-6} mm	2.32
23	403	2.78
24	44	10.57
21	38.7	11.04
22	32.7	9.55
26	13.3	9.60

Pressure at end of run No. 26 = 2.1×10^{-5} mm.

The absolute values of the slopes have no particular significance, nor are the slopes in the two tables comparable with each other, because of the way in which the magnetic field, through its effect in compelling the obliquely directed electrons to describe spiral paths, makes the actual path longer than the length of the tube by an amount hard to calculate. The results do show very clearly, however, that the value of the initial slope of the log p curves does *not* diminish as the pressure diminishes. Thus the results are in agreement with the view that dissociation occurs as a direct result of the impact of an electron on a molecule. Had the dissociation been a secondary effect such as the result of a collision between a neutral molecule and an ionized molecule which itself had been produced by electron impact, equation (6) shows that the slope of the log p curve should diminish with the pressure

(always provided that the pressure is low enough to justify the approximations between equations (5) and (6)). It may be objected that the values of the initial slopes instead of being constant at all pressures, as would be the case if the dissociation were a direct effect of an electron hitting a molecule, have a decided tendency to diminish at the higher pressures. This is easily explained by a consideration of the approximations made in passing from equation (2) to equation (3). When the pressure is such that the approximation is no longer valid, the slope of log p diminishes as p increases. Hence the results at the higher pressures are of little interest. For low values of p, the slope should become more and more constant, which is what Tables I and II show. This result is clearly and decisively against the view that the dissociation in these experiments is produced by the collision of an ionized or excited molecule with a neutral hydrogen molecule. Indeed the low pressure curves (e.g. Fig. 4*b*) by virtue of their straightness are, in themselves, sufficient to establish this result. For when $d(\log p)/dt$ is constant along a curve over which p increases fivefold, clearly equation (3) is satisfied. Had equation (6) represented the results, the curve would have been strongly concave upwards.

Threshold of the dissociation effect. To find at what voltage the dissociation effect began in these experiments, hydrogen was admitted to the apparatus to a pressure of about 4×10^{-4} mm, and the device for recording the galvanometer deflection photographically was set in motion. The accelerating voltage was increased by steps of 0.4 volt from 10 to 17 volts, each individual voltage being on for 6 minutes. There was no evidence of diminution of pressure until an accelerating voltage of 12.9 volts was reached. The rates of diminution of pressure (in arbitrary units) at different potentials are as follows :

Potential (volts) :	12.1	12.5	12.9	13.3	13.7	14.1
Diminution in pressure :	0	0	1.8	4.0	6.1	8.5

On plotting these values (which on account of the smallness of the effect are quite uncertain as to the decimal) and finding the intercept of the line with the voltage axis, we concluded that the dissociation began at about 12.55 volts. On account of contact difference of potential, fall of potential along the filament, and initial velocities of the electrons, the applied accelerating voltage may differ appreciably from the actual accelerating voltage. To find the correction the apparatus was connected up as in the usual Lenard method for determining the ionizing potential. The grid G and the coating C were connected together and various accelerating voltages were applied between them and the filament. The end plate E was connected through a delicate galvanometer to a potential 4 volts negative with respect to the filament. This ensured that nothing but positive ions (and radiation, if any) could get to E. As is well known the *strong* ionization begins in hydrogen when the electrons acquire 15.9 volts energy.[6] A strong discontinuity in the

[6] K. T. Compton and F. L. Mohler, Critical Potentials, p. 118. O. W. Richardson, Proc. Roy. Soc. **A113,** 412 (1926).

positive ion curve was therefore to be looked for in the current to E. Actually there was considerable difficulty in locating the 15.9 volt discontinuity. (This is perhaps not unexpected for the apparatus was designed for measuring dissociation and not for getting clear cut critical potentials.) In successive experiments, carried out under precisely the same conditions as the dissociation experiments, the discontinuity was located at 17.0, 16.6, and 17.0 volts, giving a mean value of 16.9 volts. If now the true value for this point be 15.9 volts, we have a correction of 1 volt. Thus our observed voltage for the onset of the dissociation, viz., 12.55 volts should be 11.5 volts.

Discussion

The evidence for the conclusion drawn in the previous section that dissociation of a hydrogen molecule is a direct result of collision between it and an electron must now be examined in more detail. That this is a direct effect is deduced from the fact that the slope of the log p curves does not diminish with decreasing pressure, or alternatively, that the log p curves fit in with equation (3) but not with equation (6). However there are conditions under which dissociation produced as a secondary effect, i.e. according to the principles underlying equation (6) might give an experimental result apparently in agreement with (3). Let us suppose that the primary effect is the formation of an ionized (or excited) molecule, which, on colliding afterwards with a neutral molecule, dissociates it, or is dissociated. If the geometrical conditions and the pressure were such that the mean free path of the electron were considerably less than the path of the electron in the apparatus, while that of the ionized (or excited) molecule were decidedly smaller than its path to the wall, then in equation (4) one could replace the first expression in brackets in the denominator by d/λ or pd/β, but the same type of approximation could not be made in the second expression in brackets. On rearranging as before, we should get, instead of equation (6)

$$d(\log p)/dt = \text{const.} \times (1 - e^{-d_1/\lambda_1}) \qquad (7)$$

Now if λ_1 is much less than d_1 the expression in brackets is practically unity, and so the equation is not to be distinguished experimentally from equation (3). It is only when λ_1 is decidedly greater than d_1 that this equation becomes identical with (6). Alternatively we may explain the point at issue by saying that if the mean free path of the ionized (or excited) molecules is so small, above a certain pressure, they practically all collide with neutral molecules and dissociate them, and so the yield of dissociated molecules will be practically the same as the number of collisions between electrons and molecules giving rise to ionized (or excited) molecules. Thus it will be impossible to decide from the dissociation produced at different pressures whether it happens as a direct or as a secondary effect.

Smyth[7] and Dempster[8] have shown that the mean free path of an ionized hydrogen molecule is ten to fifteen times less than that of a neutral molecule.

[7] H. D. Smith, Phys. Rev. **25**, 461 (1925).
[8] A. J. Dempster, Phil. Mag. **3**, 115 (1927).

Presumably an excited molecule must have a mean free path somewhere between that of an ionized molecule and that of a neutral molecule. This of course diminishes the pressure range over which the experimental test has any validity. We have now to calculate the number of ionized (or excited) molecules reaching the walls without collision. For simplicity we suppose that the electrons travel down the axis of the tube and that the ionized (or excited) molecules are produced here. From this axis, the mole-

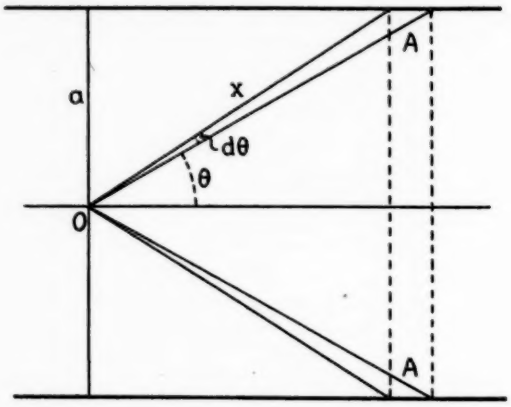

Fig. 5.

cules may be assumed to move in random directions. The number of molecules starting from O, and reaching the circular ring A on the tube (Fig. 5) without collision is

$$\tfrac{1}{2}N \sin\theta \, d\theta \, e^{-x/\lambda}$$

where N is the total number emitted from O in all directions. The total number reaching the walls without collision is

$$N' = 2\int_0^{\pi/2} \tfrac{1}{2}N \sin\theta \, d\theta \, e^{-a/\lambda \sin\theta} d\theta = NK$$

where K is the definite integral. The total number reaching the walls without collision, *if we assume them all to go the shortest distance a*, would be

$$N'' = Ne^{-a/\lambda}$$

The integral was calculated graphically for various ratios of a to λ and the results are summarised as follows:

TABLE III

λ :	$0.5\,a$	$1\,a$	$2\,a$	$4\,a$	$8\,a$
N'/N'':	0.585	0.745	0.835	0.890	0.920

The ratio N'/N'' is to be regarded as a sort of obliquity factor. The foregoing calculation is necessary before we can apply the equation (7). In this

we require what may be called the "effective mean free path," λ_1, for calculating the number of collisions $(1-e^{-d_1/\lambda_1})$ in which it would not be correct to use the actual mean free path, and $d_1=1$ cm, the radius of the tube. In the following calculations, having assumed a certain definite value for the mean free path for an ionized (or excited) molecule, we then compute the effective mean free path by interpolation from Table III and use this to calculate the number of collisions $(1-e^{-d_1/\lambda_1})$. Taking the mean free path of the normal hydrogen molecule as 0.0143 cm at 1mm pressure, and making the assumption that the mean free path of the ionized molecule is one tenth of this, viz., 0.00143 cm at 1 mm pressure, we compute the actual mean free path for several pressures in the second column of Table IV. In the third column we have the (interpolated) values from Table III for the obliquity factor. In the fourth column we record the effective mean free path λ_1 and the rest is self evident.

TABLE IV

Pressure (mm)	λ (cm)	Obliquity factor correction	Corrected $\lambda=\lambda_1$ (cm)	d_1/λ_1	$(1-e^{-d_1/\lambda_1})$
A. Mean free path, λ, at 1 mm = .00143 cm (1/10 normal)					
5×10^{-4}	28	.97	27.0	.038	.037
10	14	.95	13.3	.075	.073
20	7	.92	6.38	.157	.145
40	3.5	.88	3.08	.325	.277
80	1.9	.82	1.56	.640	.473
160	.95	.73	.685	1.460	.768
320	.47	.54	.254	3.92	.980
B. Mean free path, λ, at 1 mm = .000143 cm (1/100 normal)					
5×10^{-4}	2.8	.87	2.42	.415	.34
10	1.4	.79	1.10	.915	.60
20	.7	.67	.47	2.14	.88
40	.35	.45	.14	7.14	1.00
80	.19	.27	.05	20	1.00
C. Mean free path, λ, at 1 mm = .000048 cm (1/300 normal)					
2.5×10^{-4}	1.88	.82	1.54	.65	.478
5	.94	.73	.685	1.46	.768
10	.47	.54	.254	3.92	.980
20	.235	.34	.078	12.7	1.000
40	.122	.15	.018	55.5	1.000
80	.061	.05	.000	∞	1.000

Returning to equation (7), we see (from Table IV) that the factor $(1-e^{-d_1/\lambda_1})$ is practically proportional to the pressure from 5×10^{-5} mm to 40×10^{-5} mm and nearly so from 40×10^{-5} to 160×10^{-5} mm. Conquently if the mean free path of the ionized (or excited) molecule is ten times that of the neutral molecule, the initial slopes of the various log p curves should diminish with the pressure, provided the pressures are below about 200×10^{-5} mm, (making an arbitrary assumption that a 20 percent change in slope is well outside experimental error and is therefore to be taken as a decisive criterion).

If the mean free path of the ionized molecule be 100 times less than that of the normal molecule, section *B* of Table IV shows that the initial slopes

of the log p curves should diminish with the pressure provided that the pressure were below about 17×10^{-5} mm, while above 30×10^{-5} mm, they would become independent of the pressure.

Finally if the mean free path of the ionized molecule were assumed to be 300 times less than that of the normal molecule, section C of Table IV shows the initial slopes of the log p curve would change with the pressure below 6×10^{-5} mm, while at pressures above that value they should be practically the same at all pressures.

Referring now to the experimental results given in Tables I and II, it is evident that below initial pressures of about 50×10^{-5} mm, the initial slopes of the log p curves are independent of the pressure. The foregoing discussion then indicates that, if the mean free path of the ionized (or excited) molecule be not less than one tenth of the normal mean free path, the constancy of the initial slopes of the log p curves makes it impossible to account for the effect by the postulated secondary process. If we assume that the mean free path of the ionized molecule be 100 times less than normal, we can prove the absence of the postulated secondary process only by consideration of the last three lines in Table I and the last two lines in Table II, because the initial slopes would be constant anyhow with the assumed mean free path for pressures above about 20×10^{-5} mm.

To prove that the secondary process as described cannot be the cause of the dissociation even though the mean free path be 300 times less than normal, we can no longer appeal to the constancy of the various initial slopes in the lower parts of Tables I and II, because the foregoing considerations show that they would be constant, whichever process took place, above a pressure of about 6×10^{-5} mm. However we can use the curves corresponding to the two lowest runs taken, (one for 100 volt electrons, and one for 20 volt electrons) to decide definitely against the secondary effect process. One of these curves is reproduced in Fig. 4*b*. It will be seen that it is perfectly straight from beginning to end, the corresponding pressures being 13.3×10^{-5} mm to 2.1×10^{-5} mm. We have already seen that, below a pressure of about 6×10^{-5} mm, the slope of the log p curve should be strongly curved if the dissociation comes about as a result of an impact of an ionized (or excited) molecule on a neutral molecule, even though its mean free path is 300 times less than normal.

The final conclusion to be drawn from these considerations is that, if the dissociation of the hydrogen through which electrons are driven is a secondary process in which the electron first ionizes (or excites) a molecule, which, later, on collision with a neutral molecule, is dissociated, the mean free path of the ionized (or excited) molecule must be at least 300 times smaller than that of the neutral molecule. Since all estimates of the mean free path of the ionized hydrogen molecule range between one tenth and one fifteenth that of the normal molecule, we are justified in assuming that the dissociation of the hydrogen molecule is not a secondary process of the kind postulated. The dissociation is therefore probably the direct result of the impact of the electron on the molecule.

The results of these experiments are in accord with the conclusions of Blackett and Franck[9] and of Lowe[10] as to the origin of the Balmer lines when an electron stream passes through hydrogen at very low pressures. Lowe measured the intensities of the Balmer lines and the principal secondary lines as a function of the pressure. For electrons of energy above 50 volts, he found that, for all lines, whether of atomic or molecular origin, the intensity was strictly proportional to the pressure. Had the atomic lines been the result of a secondary effect such as the collision with a neutral molecule previously ionized or excited by an electron impact, their intensities should increase more rapidly than the pressures. Consequently Lowe inferred that the dissociation of the molecule was a direct result of electron impact. At lower energies of impact, Lowe found that the intensities of the Balmer lines were not strictly proportional to the pressure although strict proportionality was found for a large number of secondary lines. He suggests that here we may have a mixture of atoms produced by direct impact with a measurable number of atoms produced by secondary effects, the proportion of the latter diminishing rapidly as the energy of impact of the electrons is raised. There were certain lines of the many lined spectrum whose intensity-pressure curves departed from linearity more than the Balmer lines. Hence it would appear that, if under low impact energies a portion of the atomic spectrum arises from secondary effects, then certain lines of the many lined spectrum also arise, in part at least, from secondary effects. (The slight difference between the behavior of the lines with high and low energies of impact in Lowe's experiments led the authors to work at both 100 volts and 20 volts.) In addition to showing that the intensities in the atomic and molecular spectra increase with the pressure in the same way, Blackett and Franck found that the emission of the light was confined to the path of the electrons in the rarefied hydrogen. This they took to indicate definitely that the excitation of the series lines, and therefore the dissociation of the molecule, arose in the same way as the excitation of the many lined spectrum, that is, by direct electron impact. Had the collisions with neutral molecules of the ionized (or excited) molecules diffusing from the electron path into the neighboring regions been the source of the atomic radiation, it would have come from a larger, less well defined region than it did. It was also argued that, in hydrogen at 1/100 mm pressure, since the average time between collisions is 500 times that of the life of the excited atom there would be practically no radiation of atomic lines unless they were due to dissociation of the molecule as a direct result of electron impact. (It should be said that Blackett and Franck did not work with energies of impact below 30 volts, and so perhaps did not observe the effect noticed by Lowe which was marked at 25 volts but only just perceptible at 35 volts.)

The significance of where the dissociation apparently begins in these experiments is not very clear. Even if we assume a possible error of ± 1 volt, the point at which dissociation first appears, viz., 11.5 volts, is well below

[9] P. M. S. Blackett and J. Franck, Zeits. f. Physik **34**, 389 (1925).

[10] P. Lowe, Trans. Roy. Soc. Canada (3) vol. **20**, section III, 217 (1926).

the sum of the energies necessary to dissociate a molecule and to excite one atom which are respectively 4.3 and 10.2 volts, giving a total of 14.5 volts. Rusk,[11] in his study of the disappearance of hydrogen in a potassium arc, concludes that dissociation begins at 16.0 volts. On the other hand, Glockler, Baxter, and Dalton[12] show that hydrogen in contact with copper oxide begins to disappear when electrons of energy 11.4 volts are driven through the gas. This, because of its close agreement with the 11.6 volt excitation potential of the hydrogen molecule, leads them to attribute the disappearance of the gas to the chemical action between the "activated" hydrogen molecule and copper oxide.

We may classify the possible combinations of effects which may happen as a direct result of a collision between an electron and a hydrogen molecule as follows :

(1) Ionization without dissociation, H_2^+
(2) Ionization with dissociation, H^+
(3) Excitation without dissociation H_2'
(4) Excitation with dissociation, H'

These dissociation experiments indicate that either both or one of the effects (3) and (4) are present as direct results of electron impact on hydrogen molecules. The positive ray experiments of Dempster, Smyth, and Hogness and Lunn rule out effect (2). We therefore can get dissociation only in conjunction with excitation, that is, effect (4). Smyth [13] has criticised this interpretation and Hogness and Lunn[14] take the very natural view that inasmuch as ionization is to be regarded as merely the limiting case of excitation, there is no reason to believe that effect (4) happens when effect (2) does not happen. It is therefore necessary to consider carefully any possible alternative to effect (4) which would also lead to the slope of the log p curves being independent of the pressure. If the ionized (or excited) molecule condensed on the surface and stayed there, then the diminution in pressure would be indistinguishable from the diminution in pressure arising from dissociation by direct electron impact. If the ionized molecules stuck on the surface as such, they would soon build up a field sufficient to bring the electron current to zero. If they gave up their charges, they would presumably behave exactly like any neutral hydrogen molecule and not stay on the surface. It has been shown[15] that the dissociation yield is always greater than the yield of positive ions per collision and hence whether or not the positive ions on hitting the surface give rise to the dissociation, they cannot account for all of it. There remains the possibility that a metastable hydrogen molecule produced in the electron path travels to the walls. It may return to the normal state here or it may break up into two

[11] R. Rusk, Phys. Rev. **25,** 889 (1925).
[12] G. Glockler, W. P. Baxter, and R. H. Dalton, Jour. Am. Chem. Soc. **49,** 58 (1927).
[13] H. D. Smyth, Phys. Rev. **25,** 464 (1925).
[14] T. R. Hogness and E. G. Lunn, Phys. Rev. **26,** 44 (1925).
[15] A. Ll. Hughes, Phil. Mag. **48,** 59 (1924).

atoms which fly apart and condense elsewhere on the cold walls. In the latter case, the way in which the slope of the log p curves depends on the pressure would be identical with that when dissociation is produced by direct impact. Consequently our experiments, strictly speaking, only disprove the possibility of dissociation arising from impact of an ionized (or excited) molecule on a neutral hydrogen molecule. They do not establish with equal certainty that dissociation *must* arise as an immediate result of the impact of an electron on the molecule. In strong support of this view however we have the experiments of Blackett and Franck, and of Lowe, already discussed, which show that dissociation as evidenced by atomic lines, occurs in the path of the electrons. Moreover the life of an excited molecule is generally considered to be of the order of 10^{-7} second which is far too short an interval of time to allow the molecule struck by the electron to get to the walls before returning to the normal state. While we possess evidence of the existence of certain long lived metastable atoms (e.g. mercury in 2^3P_0 state) there is no direct evidence known to the authors for the existence of metastable hydrogen molecules as distinguished from excited hydrogen molecules. Even if the metastable molecule existed long enough to hit the walls, there is still the question to be considered whether they would return to the normal state there, or stay there indefinitely as metastable molecules, or fly apart, the atoms condensing separately elsewhere.

WASHINGTON UNIVERSITY,
ST. LOUIS, MISSOURI.
April, 1927.

THE POSITIVE RAY ANALYSIS OF NITRIC OXIDE AND COLLISIONS OF THE SECOND KIND

By T. R. Hogness and E. G. Lunn

Abstract

Using an apparatus previously described, in which ions formed by impact of electrons of definite energy are analyzed by Dempster's positive ray method, the relative numbers of the ions NO^+, N^+ and O^+ were measured over a large range of pressures and electron energies. The percentages of N^+ and O^+ increased gradually with increase in pressure from approximately 4 and 1.5 percent at zero (extrapolated) pressure to 9 and 3 percent, respectively, at 0.01 mm. Evidence is thus given that impact electrons of sufficient energy can ionize the molecules forming NO^+ ions some of which spontaneously dissociate forming N^+ and O^+, and others of which are disrupted on collision with gas molecules into the atomic ions. The ionization potentials for the formation of NO^+, N^+ and O^+ were found to be 9, 21 and 22 volts, respectively. The second, together with the ionization potential of the oxygen atom, gives 7.5 volts (175,000 cal. per mol) for the heat of dissociation of nitric oxide.

In mixtures of NO and A and of NO and He, increase in the relative intensities of NO^+ with increase in pressure gave definite evidence of collisions of the second kind: $NO+A^+=NO^++A$ and $NO+He^+=NO^++He$.

SINCE the discovery, by Franck, of collisions of the second kind, numerous experiments have given evidence of energy interchange in collisions of excited with normal atoms and molecules. To this the present paper adds evidence, from positive ray analysis, of second kind collisions involving collisions of ions with neutral molecules, the energy interchange being here accompanied by an electron transfer. The paper also discusses the positive ray analysis interpretation of the electron impact ionization of NO in continuation of a series of studies by the authors.[1] Reference thereto may be made for details of the apparatus and experimental procedure.

Positive Ray Analysis and Ionization Potentials of NO

The nitric oxide was prepared by the interaction of aqueous sodium nitrite and an acid solution of ferrous sulfate, was dried with phosphorus pentoxide, and then solidified in a liquid air trap whence it was distilled into the storage reservoir.

Positive ions. The products of ionization were found to be NO^+, N^+, and O^+. The relative numbers of these ions vary slightly with the pressure, as is shown by Fig. 1, in which the percentage of each of the ions (as measured by the relative heights of the peaks $m/e=30$, 14 and 16, respectively) are plotted as ordinates, the pressure as abscissas. Since the N^+ and O^+ curves extrapolate to finite quantities at zero pressure, evidence is given that in nitric oxide electron impact with 60-volt electrons can result either

[1] Hogness and Lunn, Proc. Nat. Acad. Sci. **10**, 398 (1924); Phys. Rev. **26**, 44 (1925); **26**, 786 (1925); **27**, 732 (1926).

in the formation of the molecular ions or in the dissociation of the molecules with the formation of atomic ions. Further, since N^+ and O^+ ions are both observed with impact electrons having velocities too small to dissociate a molecule and ionize, simultaneously, both of its atoms (see below), it follows that:

$$NO = NO^+ + \epsilon \quad (1)$$
$$NO = N^+ + O + \epsilon \quad (2)$$
$$NO = O^+ + N + \epsilon \quad (3)$$

all occur as independent primary processes and that (2) is more probable than (3), the probability of (1) being, of course, the greatest.

But the slope of the curves in Fig. 1 shows the occurrence of secondary processes of ionization, the nature of which is indicated by other results. In his work on hydrogen, Smyth[2] observed two peaks having apparent m/e ratios of 1/2 and 3/2. He attributed these to the disruption, on collision

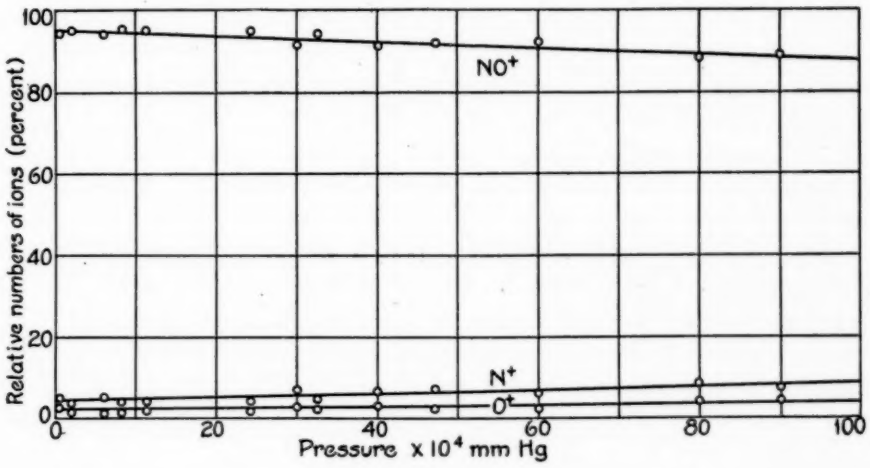

Fig. 1. Percentages of NO^+, N^+, and O^+ as functions of the pressure.

with gas molecules, of the molecular ions H_2^+ and H_3^+ which had fallen through the full positive ray analyzing field. If such a process occurred in NO the products of disruption—N^+ and O^+—would appear as peaks having m/e's of 6.53 and 8.53. A search for such ions at a pressure of 0.01 mm showed a broad band extending roughly from masses 9.5 to 5 and coming to a definite peak near 6.5. While this result only shows the instability toward collision of NO^+ ions with a velocity of 650 volts, slow speed ions may also be unstable. If NO^{++} ions disrupt in the ionization chamber, the N^+ and O^+ would, of course, appear with the peaks $m/e = 14$ and 16 which were measured for Fig. 1. It seems probable, then, that some of the NO^+ ions are unstable toward collision with gas molecules, and on collision dissociate into either N^+ or O^+:

[2] Smyth, Phys. Rev. **25**, 452 (1925).

$$NO^+ = N^+ + O + \epsilon \quad (4)$$
$$NO^+ = O^+ + N + \epsilon \quad (5)$$

and that it is these processes which cause the increase in the percentages of N^+ and O^+ with increase in pressure shown in Fig. 1. Since NO is thermodynamically unstable with respect to N_2 and O_2 and may be dissociated by the hot filament, it might be supposed, however, that some, or all, of the N^+ and O^+ ions arise from ionization of N_2 and O_2 resulting from such thermal dissociation. But the measurements of the intensities of N_2^+ and O_2^+ indicate that the partial pressures of N_2 and O_2 were far too small to account for the numbers of N_1^+ and O_1^+ ions actually observed. From their study of the ionization of NO, Bazzoni and Waldie[3] concluded that dissociation by the hot filament played such a large part in the ionization processes as to obscure the ionization due to NO itself. Thermal dissociation is minimized in the present apparatus by the rapid flow of gas, the low filament temperature and the low gas pressure.

It may be recalled that in studying nitrogen and oxygen it was not possible to establish the presence of doubly-charged molecular ions because of the identity of their specific charges and those of the corresponding atomic ions. In nitric oxide this difficulty is not met with. However, the peak at $m/e = 15$ was so small even with electron energies up to 450 volts as to make it uncertain whether it was due to NO^{++} or to an impurity. If the ion NO^{++} is formed it does not exist as such for an appreciable time.

Negative ions. With the magnetic field and the fields V_3 and V_4 reversed evidence was found of extremely small amounts of NO^-, N^- and O^-, the atomic ions being the more numerous. Because of the unfavorable arrangement of fields necessary in studying negative ions the significance of these observations is very doubtful.

Ionization potentials. The ionization potentials for the formation of NO^+, N^+ and O^+ were determined by comparing their disappearing potentials with that of argon or of helium in essentially the manner previously employed —the molecular potential by comparison with argon, the atomic potentials by comparison with helium. Taking 15.4[4] and 24.5[5] volts as the ionization potentials of argon and helium, the resulting ionization potentials for the formation of NO^+, O^+ and N^+ are 9, 21 and 22 volts respectively.[6]

The above value of 9 volts for the ionization potential of NO^+ agrees well with the more accurate values of Hughes and Dixon[7] and of Mackay,[8] 9.3 and 9.4 volts respectively.

[3] Bazzoni and Waldie, J. Franklin Inst. **197,** 57 (1924).

[4] Hertz and Kloppers, Zeits. f. Physik **31,** 463 (1925).

[5] Lyman, Science **56,** 167 (1922).

[6] The latter potentials were previously (Phys. Rev. **28,** 849 (1926)), through arithmetical error, given as 20 and 21 volts. However, the experimental error is probably greater than one volt.

[7] Hughes and Dixon, Phys. Rev. **10,** 495 (1917).

[8] Mackay, Phys. Rev. **24,** 319 (1924).

This ionization potential is that for the formation of the molecular ion (process (1)) ; the other potentials are associated with processes (2) and (3) respectively :

$$NO = O^+ + N + \epsilon \text{ ; 21 volts} \quad (4)$$

$$NO = N^+ + O + \epsilon \text{ ; 22 volts} \quad (5)$$

These, together with Hopfield's[9] values for the ionization potentials of the oxygen atom (13.56 volts) and the nitrogen atom (14.48 volts), give 7.5 volts (175,000 cal. per mole) as the heat of dissociation of NO. This is in reasonable agreement with the value of 7.9 of Birge and Sponer.[10] The one volt difference in the ionization potentials for processes (2) and (3) agrees with the difference (.92 volts) found by Hopfield for the atomic ions.

In an earlier paper we have shown that the oxygen molecule ion having 20 volts energy is unstable and dissociates spontaneously. This we explained on the basis of a recent theory of Franck.[11] This explanation was strengthened by the conclusions, from spectroscopic observation, of Birge and Sponer. The process of the spontaneous dissociation of some of the NO^+ ions is presumably substantially the same as that given for O_2^+ except that the probability of the transition to the state beyond the convergence limit of the vibrational states is not as great in the case of NO^+ as in O_2^+. The disruption of NO^+ is not to be explained in the same way as was the larger effect for nitrogen. The nitrogen molecule ion, having 24 volts energy, is unstable but, we believe, needs a rearrangement of its electron system before dissociation is possible. This is effected through collision with a second molecule. In the case of NO^+, since some spontaneous dissociation does take place, the collision perhaps merely serves to give the requisite vibrational energy to cause disruption of those NO^+ ions which, immediately after their formation by electron impact, did not possess sufficient energy of vibration to disrupt spontaneously.

Nitric oxide conforms to the rule previously given that molecules with "odd" electrons have low ionization potentials. The NO molecule has one "odd" electron and, compared with other diatomic gases, has a very low ionization potential.

Collisions of the Second Kind Involving Ions

In an investigation incidental to the positive ray analysis of NO we have sought evidence for collisions of the second kind involving ions instead of excited atoms or molecules. To this end the ionization in equimolal mixtures of NO and A and of NO and He was studied. The gas mixtures were ionized with 60-volt impact electrons and the relative numbers of NO^+ and A^+ in the one case and of NO^+ and He^+ in the other were determined as a function of the total pressure. The results are given in Fig. 2 in which the circles

[9] Hopfield, Phys. Rev. **21**, 710 (1923).
[10] Birge and Sponer, Phys. Rev. **27**, 641 (1926).
[11] Franck, Trans. Faraday Soc. (1925).

represent the observed percentages of the NO^+ and A^+ ions from an approximately equimolal mixture of NO and A, the crosses, similarly, the observed percentages of the NO^+ and He^+ ions from an approximately equimolal NO–He mixture. If these ions were formed only by the primary process of

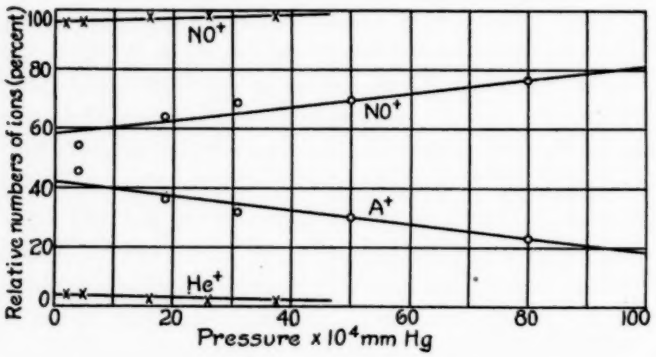

Fig. 2. Percentages of the respective ions from NO-A and NO-He mixtures as functions of the pressure.

electron impact these four curves would, obviously, be straight lines parallel to the axis of abscissas. The observed change in the relative numbers of the two different ions with increase in pressure gives, then, definite evidence for a type of collision of the second kind in which the ion robs the molecule of one of its electrons:

$$A^+ + NO = NO^+ + A \qquad (6)$$

$$He^+ + NO = NO^+ + He \qquad (7)$$

Since the potentials for the formation of A^+ and He^+ are higher than the ionization potential of NO, the processes (6) and (7) take place with evolution of energy—as radiation, kinetic energy or both. Smyth and Harnwell[12] have observed this same type of second-kind collision in He-Ne and A-Ne mixtures.

DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA,
April 11, 1927.

[12] After beginning this aspect of our studies we learned that Smyth and Harnwell of Princeton University were investigating the same general problem. As a result of correspondence with them a preliminary report embodying the results of both laboratories was published, jointly, in Nature, Jan. 15, 1927.

ON DIELECTRIC CONSTANTS AND MAGNETIC SUSCEPTIBILITIES IN THE NEW QUANTUM MECHANICS. PART II—APPLICATION TO DIELECTRIC CONSTANTS

By J. H. Van Vleck

Abstract

1,2. The proof of the Langevin-Debye formula given in part I with the new quantum mechanics is rather abstract because of its very generality, and so the results are made more concrete and non-mathematical by discussing some of the models that are included as special cases. This general derivation shows that the Debye formula applies to asymmetrical models with three unequal moments of inertia quite as well as to the symmetrical molecules previously studied by various writers with the aid of special models. Unlike the old quntum theory, there is no abrupt change of dielectric constant with pressure or field strength due to the passage from "weak" to "strong" spacial quantization.

3. Influence of a magnetic field. The mathematical theory of part I shows that very generally a magnetic field H should be without effect on the dielectric constant (or, 4, on the refractive index, except for the Faraday and Cotton-Mouton effects) unless we consider very small terms in H^2. Recent spectroscopic data show that apparently the only feasible explanation of the absence of a "*magneto-electric directive effect*" in NO is Piccard's and de Haas' suggestion of equal numbers of "left" and "right-handed" molecules having mutually opposite senses of electronic rotation relative to the molecular axis.

4. Refractive index—effect of vibration bands. A general formula is given for the refractive index which shows that the refractivity per molecule should not vary with temperature despite "temperature rotation" of the nuclei about the center of gravity. The experimental confirmation of this fact may be regarded as verifying the sum-rules" characteristic of the new quantum mechanics. The suggestion of Debye "nd Ebert that the experimental discrepancy between n_0^2-1 and $4\pi N\alpha$ is due to infra-red nuclear vibration bands is shown to be untenable in molecules such as HCl. Here n_0 denotes the extrapolation of th e index of refraction to zero frequency from visible dispersion curves, and $N\alpha$ is the pa rt of the static dielectric susceptibility due to "induced polarization." Measurements by Bourgin and others of the intensity of infra-red absorption bands furnish values of the "effective charge" associated with the nuclear oscillations and so enable one to calculate the contribution of the vibration bands to the polarization. In HCl this contribution proves to be about 1/100 of that necessary to account for the discrepancy mentioned above.

5. Limit of accuracy of the Debye formula. Because a fraction, usually small, of the molecules have sufficiently large rotational quantum numbers to make their frequencies of rotation comparable with kT/h, the Debye formula holds only asymptotically at high temperatures in the new quantum mechanics, and at ordinary temperatures the correction for departures from the asymptotic value consists approximately in adding a very small term $-NC/T^2$ to the ordinary Debye expression $N\alpha+N\mu^2/3kT$ for $(\epsilon-1)/4\pi$. The value of C is calculated for the most general rigid asymmetrical molecule, and reduces for symmetrical molecules to the value previously obtained for them by Kronig and Manneback by an entirely different method.

6. General classical derivation of the Langevin-Debye formula. It is shown that according to classical mechanics in any multiply periodic dynamical system amenable to statistical theory the susceptibility equals $N\overline{\mathbf{M}^2}/3kT$, where $\overline{\mathbf{M}^2}$ is the statistical

mean square of the vector moment of the molecule; i. e., the average over the phase space weighted according to Boltzmann factor, which is not to be confused with the time average for an individual molecule. This formula for the susceptibility is a generalization of the Langevin-Debye formula, and reduces to the ordinary Debye expression $A+B/T$ if the dynamical system consists of a rotating elastic polar molecule executing small vibrations about an equilibrium configuration.

IN PART I[1] a very general derivation was given of the Debye formula[2]

$$\frac{3}{4\pi}\frac{\epsilon-1}{\epsilon+2}=N\left(\alpha+\frac{\mu^2}{3kT}\right) \tag{1}$$

for the dielectric constant ϵ. This proof was based on the new quantum mechanics, and assumed only that the molecule has a "permanent" dipole moment of constant magnitude μ and that the precession frequencies of the moment vector are small compared to kT/h. For a more detailed explanation of these assumptions, discussion of the conditions under which they are likely to be fulfilled, etc., the reader is referred to part I. Sections 1–4 of the present paper are, however, mainly descriptive and do not require any extensive familiarity with the mathematical analysis in part I. The term $N\alpha$ in (1) arises from the "induced polarization" and was shown in part I to be associated with "high frequency" matrix elements representing transitions from normal states to "excited states" whose energies are large compared to kT.

1. Atoms and Non-Polar Molecules

Atoms and non-polar molecules have, of course, as a rule[3] no permanent dipole moment, so that the right-hand side of (1) reduces to $N\alpha$, an expression which does not vary with temperature except through the number N of molecules/cc. This is in accord with the fact that the quotient of the left-hand side of (1) by density is ordinarily found experimentally[4] to be independent of the temperature in monatomic and non-polar gases. The value of α can be calculated exactly for monatomic hydrogen from the quantum theory of the second order Stark effect,[5] and yields a dielectric

[1] J. H. Van Vleck, Phys. Rev. **29**, 727 (1927). Referred to as part I throughout the present paper.

[2] Eq. (1) of this paper differs from Eq. (1) of part I and from the Eqs. of section 6 in having the well-known Clausius-Mosotti correction for the fact that the "local field" is not the same as the large-scale field F. See p. 729 of part I. Without this correction the left side of (1) would be simply the susceptibility $\chi=(\epsilon-1)/4\pi$.

[3] An exception to the statement that the temperature coefficient of the dielectric constant of a monatomic gas is zero at constant density occurs in case the states occupied by the atom at the temperature under consideration consist of a multiple level whose components have a separation comparable with or less than kT. This is a situation not commonly encountered in monatomic gases, but a hypothetical example, calculated by the writer (see notes 6 and 31), is monatomic hydrogen gas at temperatures so high than the electrons are in excited "fine structure" levels rather than the normal singlet level.

[4] Occasionally, however, due to molecular association or other causes, anomalous temperature variations are observed in the dielectric constants of non-polar gases. Cf., for instance, Bramley's observations on bromine, Journ. Frank. Inst., Feb. 1927.

[5] G. Wentzel, Zeits. f. Physik, **38**, 527 (1926); I. Waller, *ibid.* **38**, 635 (1926); P. S. Epstein, Phys. Rev. **28**, 695 (1926).

constant[6] 1.000229 at 0°C and atmospheric pressure. This value is, of course, very hard to check experimentally because of the difficulty of dissociating hydrogen into the monatomic form, but approximate calculations can be made of the dielectric constants of other atoms, and even of some non-polar molecules, by supposing their electronic motions to be nearly hydrogenic. The effective nucear charge for the equivalent hydrogenic atom can then be deduced from observed dielectric constants, and compared with estimates obtained by other methods. This has been done by the writer[6] for molecular hydrogen and helium, and by Pauling[7] for numerous other atoms. Especially in He and H_2 the agreement between various estimates of the nuclear charge is much better with the new than with the old quantum theory.

2. Polar Molecules

Polar molecules, of course, have in general a permanent electrical moment different from zero, and hence a dielectric constant which varies with temperature even at constant density. This is just what is found experimentally, and from observed temperature coefficients of dielectric constants it is possible to determine the electrical moment μ. The results often throw very interesting light on molecular structure. It is found, for instance, that CH_4 and CCl_4 are non-polar, whereas permanent electrical moments are observed[8] for the intermediate molecules CH_3Cl, CH_2Cl_2, $CHCl_3$ in which the carbon atom is united to two kinds of atoms instead of to four alike. In the present paper, however, no attempt will be made to discuss the numerical application of the Debye formula to the vast amount of experimental material on dielectric constants, and to thus form quantitative estimates of the dipole moments for different molecules. The requisite calculations are already available in the literature[9] for a large number of different substances, and are, of course, simply trial and error determinations of the values of the constants α and μ in Eq. (1) which yield closest agreement with the experimental temperature curves. Eq. (1) is identical with the classical formula, and so, unlike the old quantum theory (cf. p. 728, part I), the new quantum mechanics gives the same numerical dipole moments as the classical theory. It is to be clearly understood that Eq. (1) applies primarily to gases. Efforts, to be sure, have been made to apply the Debye formula to liquids, but, as emphasized by Debye[9] himself, Eq. (1) is in general valid in the liquid state only in the case of dilute solutions of polar molecules in non-polar solvents.

Our discussion of Eq. (1) will thus usually center around its general theoretical basis rather than its numerical application. In order to correlate the different theoretical derivations of (1) which have previously been given

[6] J. H. Van Vleck, Proc. Nat. Acad. **12**, 662 (1926).

[7] L. Pauling, Proc. Roy. Soc., **114A**, 181.

[8] Cf. R. Sanger, Phys. Zeits. **27**, 563 (1926).

[9] An excellent summary of the experimental work until 1924 has been given by Debye in vol. VI of the Handbuch der Radiologie. A comprehensive survey of the more recent experimental data, together with copious references to the literature, is given by O. Blüh, Phys. Zeits. **27**, 226 (1926).

for special models, we may distinguish between the four following types of molecules:

(*a*) non-gyroscopic diatomic molecules,

(*b*) diatomic molecules which are gyroscopic due to an electronic angular momentum about the axis of figure,

(*c*) symmetrical polyatomic molecules; i.e., molecules which are composed of more than two atoms but in which two of the three principal moments of inertia are equal,[10]

(*d*) asymmetrical polyatomic molecules, characterized by three unequal moments of inertia.

Probable examples of the four cases $(a)-(d)$ are respectively HCl, NO, NH_3, and CH_2Cl_2. The order of the list $(a)-(d)$ is that of increasing difficulty for calculation with special models. The general derivation of the Debye formula given in part I, however, is applicable to all four cases, for the condition imposed in part I that the molecule have a permanent moment vector whose precession frequencies are small compared to kT/h is satisfied in most of the normal states. This is true since in the first place molecules are usually rigid enough to fulfill fairly closely the demand of permanency of moment (see especially in this connection the paragraph at the end of section 6), and in the second place practically all molecules have large enough moments of inertia so that the frequencies of rotation of the nuclei about the center of gravity are small compared to kT/h except in states with abnormally large rotational quantum numbers for the given temperature. These "nuclear" or "temperature" rotation frequencies[11] can, to be sure, be made as large as we please relative to kT/h by assigning sufficiently large values to the rotational quantum numbers, but states with such large quantum numbers have a large energy W, and hence a small Boltzmann probability factor $e^{-W/kT}$, so that it is fairly apparent that their contribution may be neglected without sensible error (cf. note 26, part I). This is also demonstrated mathematically in section 5, where the error due to neglecting higher powers of $h\nu/kT$ is calculated explicitly.

(*a*) Instead of thus establishing the applicability of the general proof given in part I, one can also derive the Debye formula for the case (*a*) of

[10] It is often stated in the literature than the essential criterion for case (*c*) is an axis of symmetry, but this is incorrect if the term axis of symmetry is construed in the usual crystallographic sense of meaning that a rotation of 180° about this axis brings the system back to a configuration indistinguishable from the initial one, for this condition by no means implies two equal moments of inertia. Instead (*c*) seems usually to result from a grouping of identical atoms about the axis at corners of a regular polygon (e. g. in NH_3 the N atom is probably at the apex of a pyramid whose base is an equilateral triangle with H atoms at the corners).

[11] In dealing with dielectric constants we do not ordinarily need to consider the precessions due to internal spins of the electrons, for with very few exceptions (notably NO) the normal states of most molecules are non-magnetic. Diatomic molecules with spin moments are considered in case (*b*) below, while even polyatomic molecules with spin moments (e. g. ClO_2) are included in the general proof of the Debye formula given in part I, certainly provided the frequencies with which the spin axis precesses are small compared to kT/h, and as a matter of fact even if this condition is not met the proof may still apply, for the precessions of the spin moment probably often do not carry with them the heavy nuclear framework containing the permanent dipole moment, except for small nutations (cf. note 20).

non-gyroscopic diatomic molecules, by making the calculation directly with the amplitude matrices for the rotating dipole given by Mensing,[12] Oppenheimer,[13] Fues,[13] or Dennison.[14] Such calculations were made independently and practically simultaneously by Mensing and Pauli,[15] Kronig,[16] and the writer.[17] A variant of the computations using the wave rather than matrix method has been given by Manneback.[18] We shall give only a brief summary of case (*a*) because details are already in the literature.[15,16,17,18] An interesting result found in (*a*) but not in (*b–c–d*) nor in the old quantum theory, is that the contribution of the permanent moment to the dielectric constant; i.e., the second right-hand term of Eq. (1) or of Eq. (2) below, arises entirely from molecules in the lowest rotational state $j=0$. This is a beautiful quantum analog of the fact that classically in models of type (*a*) the corresponding "temperature" term ensues entirely[19] from the sluggish molecules having energies less than μF. The quantum mechanics show that in case (*a*) the dielectric constant is given by the simple expression

$$\frac{3}{4\pi}\frac{\epsilon-1}{\epsilon+2}=N\left(\alpha+\frac{8\pi^2 I\mu^2 N_0}{3h^2 N}\right) \tag{2}$$

where N_0 is the number of molecules in the lowest rotational state. By evaluation of the ratio N_0/N, formula (2) is readily shown to merge into (1) at high temperatures. Eq. (2), however, has the added advantage of holding even at temperatures so low that $h\nu/kT$ is comparable with unity. Eq. (1), nevertheless, is an adequate approximation at ordinary temperatures. From (2) it is seen that the susceptibility remains finite even at $T=0$, where $N_0/N=1$. In the classical theory, on the other hand, there is complete saturation at the absolute zero, and the susceptibility increases without limit for given F when T approaches zero.

(*b*) In models of type (*b*) a component of electronic angular momentum along the axis of figure makes the diatomic molecule behave like a gyroscope, and hence an approximate model[20] is furnished by the "symmetrical top"

[12] L. Mensing, Zeits. f. Physik, **36**, 814 (1926).

[13] J. R. Oppenheimer, Proc. Cambr. Phil. Soc. **23**, 327 (1926); E. Fues, Ann. der Phys. **81**, 281, (1926).

[14] D. M. Dennison, Phys. Rev. **28**, 318 (1926).

[15] L. Mensing and W. Pauli, Jr., Phys. Zeits. **27**, 509 (1926).

[16] R. d. L. Kronig, Proc. Nat. Acad. **12**, 488 (1926).

[17] J. H. Van Vleck, Nature, **118**, 226 (1926).

[18] C. Manneback, Phys. Zeits. **27**, 563 (1926).

[19] W. Alexandrow Phys. Zeits. **22**, 258 (1921); W. Pauli, Jr., Zeits. f. Physik, **6**, 319 (1921).

[20] The symmetrical top model for molecules of type (*b*) has frequently been used in band spectra (cf., for instance E. C. Kemble, "Molecular Spectra in Gases," Bull. Nat. Research Council No. 57, p. 313). We disregard the component of electronic angular momentum normal to the axis of figure, whose presence would make the top asymmetrical. We can do this because at least in NO (see part III), the normal component of electronic angular momentum (unlike the stationary normal component in the well-known Kratzer-Kramers-Pauli model for gyroscopic molecules) precesses so rapidly compared to the temperature rotation that its main effect is only to superpose a small nutation on the temperature rotation, and hence the symmetrical top is a fair approximation to the motion. A mathematical basis for regarding molecules of type (*b*) as symmetrical tops has recently been given by Landau, Zeits. f. Physik, **40**, 621 (1926), who is led essentially to the Dennison amplitude matrices by treating the interaction of nuclear rotation and electronic motions as a problem in perturbation theory.

which has been analysed in the matrix dynamics by Dennison[14] and Landau,[20] and in the wave mechanics by Reiche and Rademacher,[21] Kronig and Rabi,[22] and Debye and Manneback.[23]

(*c*) Case (*c*) is much more frequent than (*b*), as NO is about the only common example of a molecule normally of type (*b*). The polyatomic molecules characteristic of type (*c*) have two equal moments of inertia, and consequently are likewise represented by the symmetrical top model, but the angular momentum about the axis of figure is now due to nuclear rotations rather than to purely electronic motions as in (*b*). There is also the important distinction that in (*c*) there may be a large number of different possible values for the quantum number σ specifying the angular momentum about the axis of figure, whereas in (*b*) the axial component of electronic angular momentum has only one or at most a few possible values in the normal states. The Debye formula has been deduced for case (*c*) by Kronig[24] and by Manneback.[23] These writers appear to overlook the close resemblance of their calculations for (*c*) to the computations for case (*b*) which the writer previously reported, though rather sketchily, at the close of his note to Nature.[17,25] In (*b*), to be sure, we do not sum over all values of the quantum number σ mentioned above, but, as noted to the writer by Dr. Pauling, since the Debye expression is obtained in (*b*) and does not involve σ, it must hold for a gas such as that of type (*c*) which can be regarded as a mixture of molecules with different values of σ.[26]

(*d*) The general polyatomic molecule is so unsymmetrical that it would be very laborious to work out the numerical values of amplitude matrices with a concrete model,[27] and so in this case (*d*) the general proof given in

[21] F. Reiche, Zeits. f. Physik, **39**, 444 (1926); H. Rademacher and F. Reiche, *ibid.* **41**, 453 (1927).

[22] R. d. L. Kronig and I. I. Rabi, Phys. Rev. **29**, 262 (1927).

[23] P. Debye and C. Manneback, Nature, **119**, 83 (1927); also especially C. Manneback, Phys. Zets. **28**, 72 (1927).

[24] R. d. L. Kronig, Proc. Nat. Acad. **12**, 608 (1926)

[25] In his preliminary letter[17] to Nature the writer promised to publish later the details of his calculations of the dielectric constant in cases (*a*) and (*b*), which he made originally by the Dennison[14] amplitude matrices. However, the simultaneous publication by Mensing and Pauli of their computations for case (*a*) and by Kronig for (*a*) and later (*c*) makes this unnecessary as their calculations are identical in character with those reported by the writer, except for Kronig's addition of summing over σ and calculating the small correction terms in T^{-2}. Also all four cases (*a*)–(*d*) are covered by the general proof in part I, which the writer developed subsequently to his work with the Dennison model.

[26] As a corollary to calculating the dielectric constant with special models for cases (*a*), (*b*), and (*c*) a formula for the Stark effect to terms in F^2 is obtained which is the analog in the new mechanics of formulas obtained in the old quantum theory by Hettner for case (*a*) (Zeits. f. Physik, **2**, 349, 1920) and by Lessheim for case (*c*) or (*b*) (*ibid.* **35**, 831, 1926). The new formula for case (*c*) has been given by Debye and Manneback.[23] This formula was also obtained by the writer in connection with his unpublished calculations for case (*b*) (as well as qualitatively by Landau[20]). Unlike (*a*), cases (*b*–*c*) involve linear Stark effects. Manneback[23] computes the Stark effect to terms in F^2 in the old quantum theory for case (*c*) (or equally well *b*) not knowing that the calculation had already been made by Lessheim.

[27] Even in the absence of external fields the energy (not to mention amplitude matrices) can be obtained for asymmetrical molecules apparently only as a laborious series development. See E. E. Witmer, Proc. Nat. Acad. **13**, 60 (1927).

part I furnishes much the easiest derivation of the Debye formula with quantum mechanics, in fact the only derivation yet given. In the classical theory the Debye formula can be obtained fairly directly for rigid molecules even of type (*d*) by proper choice of the variables of integration, and the writer is informed that such classical derivations for the general asymmetrical molecule are contained in unpublished work of Debye[79] and of Born. An alternative classical proof is also furnished by the methods given in section 6 of the present paper. Gaseous molecules of this complex type (*d*) are fairly common. Any non-colinear triatomic molecule, for instance, ordinarily belongs to this catagory, as in general it will have three unequal moments of inertia. A common example is H_2O. It is to be clearly understood that in asymmetrical molecules the expression μ in Eq. (1) is the scalar magnitude $(\mu_u^2+\mu_v^2+\mu_w^2)^{1/2}$ of the permanent vector electrical moment, which is in general obliquely inclined relative to the three principal axes of inertia u, v, w.

Invariance of field strength, pressure, etc. It was shown in part I that the dielectric susceptibility $(\epsilon-1)/4\pi$ is invariant of the direction of the axis of quantization. Hence the dielectric constant has the same value with random orientation, in which all directions for the atom or molecule are supposed equally probable, as with spacial quantization. Hence there is no possibility of the dielectric constant varying with the field strength due to the passage from "weak" to "strong"[28] spacial quantization, one of the bugbears of the old quantum theory. Also the spectroscopic stability relations given in section 4, part I, show that in a degenerate dynamical system the susceptibility is invariant of the manner in which the degeneracy is removed,[29] and so there is no change in dielectric constant with field due to a different type of quantization in weak and strong fields.[30] Thus the dielectric constant has the same value in weak fields, where spherical coordinates are used to handle the relativity and spin corrections, as in fields strong enough to produce a linear Stark effect, where parabolic coordinates must be employed.[31]

[28] For explanation of the terms "weak" and "strong" spacial quantization, and references to the original literature on this subject, see the writer's "Quantum Principles and Line Spectra," p. 165 (Bull. Nat. Research Council, No. 54.).

[29] The discussion in part I emphasized primarily the invariance of the spacial quantization, but the mathematics in part I, especially Eq. (25), establish equally well the invariance of the sums entering in the susceptibility formula under any transformation used in treating a perturbed degenerate system.

[30] The possibility of a change with field strength due to this cause has been suggested in the old quantum theory b yP. Debye, Phys. Zeits. **27**, 70 (1926).

[31] We may here correct an error in the writer's calculation of the dielectric constant of excited hydrogen atoms (Proc. Nat. Acad. **12**, 665, 1926). This error is not found in his computation for normal hydrogen atoms, given in the same paper, which is the case of greatest interest, but it was incorrectly stated that in excited states that the "temperature term" resulting from the Boltzmann distribution factor is important only if the field is strong enough to produce a linear Stark effect. This statement is false as the writer overlooked the contribution from terms of the form given on the 2nd line of Eq. (7), part I. Instead the spectroscopic stability relations mentioned above show that, even for excited states, the dielectric constant has the same value for weak and strong fields. This means that in the formula for $\epsilon-1$ given on p. 665 of the writer's Nat. Acad. paper, the factor $f(F)$ is unity regardless of the field strength. This is gratifying, as we can now use under all conditions this numerical formula for the dielectric constant of excited states which we previously supposed valid only for strong fields.

There, of course, still remains the change in susceptibility with field strength when the field F is strong enough to produce an appreciable tendency towards saturation. This saturation effect first enters[32] when we consider terms in the susceptibility of the order F^2, and so is detectable only in very large fields.[33] The susceptibility per molecule should not change with pressure except in so far as molecular association, inter-molecular fields, etc. are involved, as they often are to a great extent in liquids. As noted by Ebert,[34] molecular susceptibilities should be approximately the same in dilute solutions, at least with non-polar solvents, as in the gaseous state. This accords with experiment, whereas in the old quantum theory we might expect strong spacial quantization in gases at low pressures and weak in gases at high pressures and in solutions.

3. Influence of a Magnetic Field on the Dielectric Constant

There has been, first and last, a great deal of speculation as to whether a magnetic field should influence the dielectric constant. The calculation given in part I shows that, unless the fields are so exceedingly large as to necessitate a study of higher order terms[35] than those ordinarily considered, a magnetic field should according to the new quantum mechanics be without effect on the dielectric constant. This follows since in the derivation of the Langevin-Debye formula given in part I we admitted the possibility of the molecule being in external fields even when the electric field F is zero. Thus Eq. (1) is unaltered when there are other fields, in particular a magnetic field, present in addition to F.

This result is not at all surprising. Using the amplitude matrices for the simple rotating dipole Kronig[16] and especially Pauling[36] have already shown that a magnetic field should not influence the dielectric constant of a non-gyroscopic diatomic molecule (type *a*, section 2). By analogy we might expect that a magnetic field would have no effect in the more complicated cases (*b–c–d*) and part I establishes mathematically that this is indeed so. The reason why the new quantum mechanics gives a null effect as generally as does the classical theory is, of course, the high degree of spectroscopic stability

[32] For greater detail on this saturation effect (especially from the classical viewpoint) see Debye, Handbuch der Radiologie, vol. VI, p. 777 ff. Debye shows that there are two terms in the susceptibility of the order F^2, one of which is the ordinary effect due to alignment of permanent dipoles and the other of which is due to the torque on the atom or molecule arising from the induced polarization. This second term has the opposite sign from the first (i. e. is positive) and is closely related to the Kerr effect.

[33] S. Ratnowsky, Verhandl. d. D. phys. Ges. **15**, 497 (1913): J. Herweg, Zeits. f. Physik, **3**, 36 (1920); J. Herweg and W. Pötzsch, *ibid.* **8**, 1 (1922). Very interesting indirect evidence for saturation is furnished by the decrease of the dielectric constants of liquids on dissolving strong electrolytes. The ions of the dissolved electrolyte saturate the surrounding molecules of the liquid and hence lower the susceptibility. See, for instance, H. Sack, Phys. Zeits. **28**, 199 (1927).

[34] L. Ebert, die Naturwissenschaften, **14**, 919 (1926).

[35] As noted to the writer by Prof. Debye, a magnetic field H might influence the dielectric constant if H were so large as to necessitate the consideration of terms in the susceptibility of the order H^2. Such an effect would be analogous to a saturation effect, and so only observable in enormously large fields.

[36] L. Pauling, Phys. Rev. **29**, 145 (1927).

characteristic of the new dynamics (section 4, part I). This is in marked contrast to the old quantum theory, in which Pauling[36] shows a magnetic field would cataclysmically change the sign of the temperature coefficient of the dielectric constant, at least in case (*a*). Also the magnitude of the induced polarization, i.e., the first right-hand term of (1) would probably depend on the type of spacial quantization in the old quantum theory, whereas part I shows it is invariant in the new mechanics.

The predicted null effect of magnetic fields of ordinary magnitude on the dielectric constants of gases is well confirmed experimentally. Weatherby and Wolf[37] show that a field of 8000 gauss does not change the dielectric susceptibility of He, O_2, or air within the limits of experimental error[38] (10% in He and .4% in O_2 and air), while Mott-Smith and Daily[39] show with about equal accuracy[38] (8% in NO and 1% in HCl) that the dielectric susceptibilities of the polar gases NO and HCl are unaffected by a field of 4800 gauss. It must not, however, be inferred that the dielectric constants of all substances are not influenced by magnetic fields. For instance, the experiments of Friedel, Jezewski, and especially Kast[40] show that the dielectric constants of certain "mesomorphic" substances (anisotropic liquids) are somewhat altered by magnetic fields, as recently emphasized by Bauer.[41] This, nevertheless, must not be regarded as disproving the theory for, as noted by Ornstein,[42] liquid crystals are likely built out of large complexes ("elementary crystals") rather than out of ordinary free molecules such as were assumed in part I.

The magneto-electric directive effect ("Richteffekt"). There is one exception to the statement made above that according to the theory given in part I a magnetic field should be without effect upon the dielectric constant. That

[37] B. B. Weatherby and A. Wolf, Phys. Rev. **27**, 769 (1926). Their experiments were undertaken partly to see whether it was possible to determine whether or not the helium atom has a magnetic moment, for Breit and Ruark suggested that in the old quantum theory the dielectric constants of atoms with a magnetic moment would because of spacial quantization be influenced by a magnetic field to an appreciable degree (Phil. Mag. **49**, 504, 1925). In the new mechanics, however, we have seen that the dielectric constant is, as suspected by Heisenberg (Zeits. f. Physik, **31**, 617, 1925), invariant of a magnetic field regardless of whether or not the atom possesses a magnetic moment.

[38] We give the percentage error in the dielectric susceptibility rather than in the dielectric constant. The error in the susceptibility is the more significant because the dielectric constants of gases are nearly unity. Consequently a high precision in measuring the dielectric constant (1 part in 500,000 for He, O_2; 1 in 100,000 for NO, HCl) is necessary to determine the susceptibilities as accurately as mentioned above.

[39] L. M. Mott-Smith and C. R. Daily, Phys. Rev. **28**, 976 (1926). The HCl molecules molecules studied by Mott-Smith and Daily would have no magnetic moment if their nuclei were at rest, but the "temperature rotation" gives the molecules a magnetic polarity, leading to spacial quantization, etc. (cf. Pauling[36]). This magnetic moment due to nuclear rotation has been directly verified experimentally for H_2O in the molecular ray experiments of Knauer and Stern, Zeits. f. Physik, **39**, 780 (1926).

[40] E. Friedel, Comptes Rendus, **180**, 269 (1925); Jezewski, Journ. de Phys. **5**, 59 (1924); W. Kast, Ann. der Physik, **73**, 145 (1924).

[41] E. Bauer, Comptes Rendus, **182**, 1541 (1926).

[42] L. S. Ornstein, Zeits. f. Physik, **35**, 394 (1926); Ann. der Physik, **74**, 445 (1924).

exception is in case there is what may be called a "magneto-electric directive effect." By this term is meant a state of electric polarization produced by application of a magnetic field, or vica versa. The electric polarization in the magneto-electric effect is caused by alignment of molecules in the magnetic field, and if present would exist even when there is no applied electric field F. Mathematically stated, the directive effect exists if the first line of Eq. (5), part I, does not vanish when it is assumed that a magnetic field is already present in the electrically unperturbed state $F=0$. The effect is possible only if the molecule has non-vanishing and non-perpendicular magnetic and electric moments, for in the perpendicular case there is no necessary coordination between the directions of electric and magnetic polarizations. In a certain sense even the magneto-electric directive effect does not change the dielectric constant, as the mathematics in section 3, part I, shows that it does not affect the change in polarization $P-P_0$ produced by the electric field, but only introduces a residual polarization P_0 present when $F=0$. Thus the dielectric constant is unaltered if it is defined as $1+4\pi(P-P_0)/F$, but becomes infinite at $F=0$ if defined as $1+4\pi P/F$.[43]

Actually experiments endeavoring to detect a magneto-electric effect yield a null result,[44] even in liquids and solids. The only important gas in which such an effect might be expected is NO, for nitric oxide is the only common polar paramagnetic gas.[45] Hence NO has been studied experimentally with special care by Huber,[46] and has also been discussed theoretically by Debye and Huber.[47] The only way to explain the null result obtained experimentally for NO even when liquefied, is probably to assume that electronic rotations may be either clockwise or counter-clockwise with reference to the molecular axis, which we may imagine drawn from the N atom towards the O atom in order to endow this axis with sense as well as direction.

[43] Theoretically if there is a magneto-electric effect a magnetic field might slightly alter the dielectric constant defined even as $1+4\pi(P-P_0)/F$, for the denominator of the first line of Eq. (5), part I, involves the electric field F through the exponents in the exponential factors. Hence the first line, multiplied by F to give the polarization, changes on application of F, and makes a contribution to $P-P_0$. This contribution, however, is insignificant (of the same order as the effect mentioned in note 35) since the alteration in energy caused by application of F is small compared to kT, and since even with a magneto-electric effect the numerator of the first line of Eq. (5), part I is only of the order H^2. Instead $(P-P_0)/F$ results almost entirely from the second and third lines of Eq. (5), part I, which are independent of a magnetic field.

[44] Perrier and Borel, Archives des Sciences, **7**, 289 and 375 (1925); Szivessy, Zeits. f. Physik, **34**, 474 (1925); Huber, Phys. Zeits. **27**, 619 (1926).

[45] Although NO is the only important paramagnetic polar molecule, a non-paramagnetic polar molecule (e. g., HCl) acquires some magnetic moment due to nuclear rotation (cf. note 39). One at first thought wonders whether this might not cause a magneto-electric directive effect. This effect, however, would obviously be very small, although the smallness of the magnetic moment might be partially offset by the electrical moment being large compared to that in NO. Furthermore in non-gyroscopic diatomic molecules the magnetic moment due to nuclear rotation is perpendicular to the electrical moment, making the effect vanish entirely. In polyatomic molecules there might not be this perpendicularity, but as there are both left and right-handed directions for nuclear rotation there should be on the average no necessary coordination between the directions of electric and magnetic polarizations.

[46] A. Huber, Phys. Zeits. **27**, 619 (1926).

[47] Debye and Huber, Physica, **5**, 377 (1925); Debye, Zeits. f. Physik, **36**, 300 (1926).

This suggestion was made by de Haas in a letter to Debye,[48] and also previously, though in connection with solids rather than NO, in a brief note by Piccard.[49] There should then be two kinds of NO molecules, one in which the component of magnetic moment along the axis of figure has the same sense as the electrical moment, and one in which this component has the opposite sense. These two kinds of molecules differ only in being what one might term "left-handed" and "right-handed," and, since their energies are virtually identical, statistical mechanics requires that they be present in equal amounts. There is thus on the average no correlation between the directions of electric and magnetic moments, and hence no magneto-electric effect. This idea of left and right-handed molecules does not appear unreasonable to the author, who reached independently the same conclusions as de Haas. Critical molecular ray experiments have been proposed by de Haas[48] to test directly the existence of two kinds of NO molecules. Our knowledge of the structure of the NO molecule is now too precise to permit adoption of the suggestion of Bauer[41] or Weigle[50] that the null effect is due to the magnetic and electric moments being at right angles; for band spectrum data of Jenkins, Barton, and Mulliken[51] indicate pretty definitely a component of electronic angular momentum along the axis of figure, as does also the numerical analysis of the paramagnetism of NO to be given in part III.[52]

4. Refractive Index—Effect of Vibration Bands

Hitherto we have been dealing with the dielectric constant for constant fields. It is, however, easy to develop the analogous theory for the refraction of light, as it is not difficult to carry through the mathematical analysis of part I with the modification that the impressed field is assumed periodic in the time instead of constant. The basic formula for the perturbation produced in an individual atom or molecule by an impressed periodic wave, has been given by Born, Heisenberg, and Jordan,[53] and by Schroedinger.[54] This formula is, of course, essentially the Kramers dispersion formula, and is the generalization of Eq. (3), part I, which applied only to constant fields. The mathematical work corresponding to that of part I consists in getting the total polarization from the totality of molecules distributed statistically among the component levels constituting the normal states. There is a noteworthy simplification compared to the calculation with a constant field;

[48] Cf. Huber, Phys. Zeits. **27**, 625–626 (1926).

[49] Piccard, Archives des Sciences, **6**, 404 (1924).

[50] J. J. Weigle, Phys. Rev. **29**, 362 (1927).

[51] Jenkins, Barton, and Mulliken, Nature, **119**, 118 (1927).

[52] We may note parenthetically that a possible explanation of the absence of the magneto-electric effect in some substances is that the magnetic moment arises entirely from internal spins of the electrons. The alignment of the spin axes in a magnetic field then might not involve orientation of the molecular framework carrying the electric moment. This suggestion is feasible only when the normal states of the atoms or molecules are *S*-terms, but the gyromagnetic effect seems to indicate that this is quite often the case in solids. The suggestion is inapplicable to NO, as its normal levels are *P*-terms.

[53] Born, Heisenberg, and Jordan, Zeits. f. Physik, **35**, 572 (1926).

[54] E. Schroedinger, Ann. der Physik, **81**, 109 (1926).

viz., if the impressed frequency ν_0 is large compared to kT/h, a condition practically always met at ordinary wave-lengths, we can disregard entirely the contribution of the "low frequency elements" in the terminology of part I,[55] and so the mathematics consist only in averaging over the different spacial orientations with the aid of the spectroscopic stability formulas given in section 4, part I, and in showing by the "sum-rule" that the various component levels constituting the normal states give equal high frequency contributions. We omit details of the analysis, because they can readily be supplied by readers who understand the calculation in part I. The formula for the index of refraction n is found to be

$$\frac{3}{4\pi}\frac{n^2-1}{n^2+2}=\frac{2N}{3h}\sum_{n'(n'\neq n)}\frac{\nu(n\,;\,n')\,|M(n\,;\,n')\,|^2}{\nu_0{}^2-\nu(n\,;\,n')^2}, \tag{3}$$

as the right-hand side of this equation is readily shown to be the proper, as well as very obvious, generalization of Eq. (17), part I to a periodic rather than constant field. The notation in (3) is the same as in Eq. (17), part I, and thus the expressions $\nu(n\,;\,n')$, being absorption frequencies, are all negative. The important thing about Eq. (3) is that it does not contain the temperature except through N, in agreement with the well-known experimental fact[56] that the refractivity per molecule for visible light usually does not vary with temperature, unlike the dielectric susceptibility of polar gases at infinite wave-lengths. The invariance of the molecular refractivity of the temperature in non-monatomic gases appears usually to be considered as something axiomatic not requiring theoretical proof[57] despite the "temperature rotation" of the nuclei, etc., but in reality it may be regarded as an interesting experimental check on the sum-rules and spectroscopic stability.

The remarks previously made about independence of dielectric constants of magnetic fields, pressure, field strength, etc., of course apply equally well to refractive indices. A possible exception to the statement occurs when the impressed frequency is close to an absorption frequency of the atom or molecule, for then Eq. (3) fails. Also the refractive index may vary with the temperature near an absorption band, as alteration of the temperature may change the concentration of atoms in the particular component state which resonates closest to the impressed frequency. It is clearly to be understood that even in the new mechanics there is still the familiar Faraday rotation of the plane of polarization in a longitudinal magnetic field, and also an extremely intense magnetic field will produce a slight distortion in the dispersion and a double refraction such as is involved in the classical Cotton-

[55] The reason why we can disregard the low frequency elements $(njm;\ nj'm')$ in an impressed field of high frequency ν_0 is that in such a field the low frequency elements contribute terms to the polarization of the order $(\nu(njm;\ nj'm')/\nu_0)^2$ times those in the case of a constant field.

[56] Cf. especially recent experiments by E. W. Cheney, Phys. Rev. 29, 292 (1927).

[57] A proof that in the classical theory the optical refraction is independent of the temperature despite the nuclear rotation of the molecules will be published in the Madison lectures of Prof. Debye.

Mouton effect.[58] The latter effect, however, is analogous to the Kerr effect, and hence quadratic in H^2, or beyond the scope of the present paper (cf. note 35). In the old quantum theory, on the other hand, spacial quantization in a relatively small magnetic field would cause optical dissymmetry and a large double refraction not found experimentally.[59]

Relation of dielectric constant to index of refraction. In a non-magnetic medium the dielectric constant equals the square of the index of refraction for infinitely long wave-lengths. However, we have already seen above that the permanent dipole moment of the molecule, which is responsible for the "low frequency elements," makes an appreciable contribution to the polarization only at very long wave-lengths, and so influences the shape of the dispersion curve only in the far infra-red. Therefore we should expect the extrapolation of the dispersion curves made for visible light to infinitely long wave-lengths or zero frequency to yield a value n_0^2 for the square of the index of refraction which equals only the part of the dielectric constant due to "high frequency elements" or "induced polarization." In other words we should have $n_0^2-1=4\pi N\alpha$, as can also be seen by comparing the extrapolation of (3) with Eq. (17), part I. Here and in the remainder of the present section we for simplicity neglect the small Clausius-Mossotti correction, so that we disregard the factor $3/(n^2+2)$ in (3) and the analogous factor in (1).

Actually n_0^2-1 often does not agree with the value of $4\pi N\alpha$ determined from measurements of dielectric constants. For instance, in HCl at 0°C and atmospheric pressure, Zahn[60] finds $4\pi N\alpha=.001040$, whereas Cuthbertson and Cuthbertson[61] find that $n^2-1=.000888$ for illumination by sodium *D*-light, and the extrapolation to infinite wave-lengths by their Sellmeier dispersion formula gives $n_0^2-1=.000871$.

The following explanation of discrepancies such as that mentioned in the preceding paragraph has been tentatively suggested by Debye,[62] Ebert,[34] and others. Besides the "electronic" absorption frequencies (i.e. "electron transitions" in the quantum theory), and besides the pure rotation spectrum, which is in the far infra-red and corresponds to the polarization due to permanent dipoles, we must consider the "vibrational spectrum" arising from nuclear oscillations. The latter spectrum is usually located in the infra-red, and is far enough removed from the visible so that it does not introduce any irregularity in ordinary dispersion curves for visible light. Consequently extrapolation of these curves to infinite wave lengths does not include the contribution of the vibrations to the polarization. If the dispersion curve could be carried through the infra-red, the refractive index should rise to a maximum at resonance with vibrational frequencies and should then decrease

[58] A. Cotton and H. Mouton, Journ. de Phys. **1**, 5 (1911); Ann. de Chim. et Phys. **19**, 153, **20**, 194 (1910); cf. P. Debye, Handbuch der Radiologie, vol. VI, pp. 754 and 769.

[59] Cf. O. Stern, Zeits. f. Physik, **7**, 249 (1922); R. Fraser, Phil. Mag. **1**, 885 (1926); W. Schütz, Zeits. f. Physik, **38**, 853 (1926).

[60] C. T. Zahn, Phys. Rev. **24**, 400 (1924).

[61] C. and M. Cuthbertson, Phil. Trans. Roy. Soc. **213A**, 1 (1913).

[62] P. Debye, Handbuch der Radiologie, vol. VI, p. 620.

to a value at infinite wave-lengths which is greater than the value n_0^2 obtained by extrapolation of smooth curves taken only in the visible region.

A mathematical expression for this vibrational effect is easily obtained for diatomic molecules. Let m be the effective mass for the vibrations, which is $m_1m_2/(m_1+m_2)$, where m_1, m_2 are the masses of the two nuclei. Let q be the "effective charge," which is the factor by which we must multiply the amplitude of oscillation to get the corresponding change in moment. More precisely, q is the coefficient of the linear term in the series development $p=\mu+q(r-r_0)+\cdots$ of p in terms of $r-r_0$, where p is the electrical moment averaged over the rapid, purely electronic periods and where r is the nuclear separation, and r_0 is the equilibrium value of r. Now usually nuclear vibrations are small enough so that they may be represented quite approximately by a harmonic oscillator of frequency ν. The vibrational susceptibility, or quotient of polarization by field strength, is then

$$Nq^2/12\pi^2m(\nu^2-\nu_0^2) \tag{4}$$

Classically (4) is obtained immediately by making the well-known elementary calculation of the polarization due to a harmonic oscillator; (4) is, however, 1/3 as great as the usual Drude expression, since the nuclear vibrations are only along the molecular axis, whose orientation is random, and so represent one degree of freedom rather than three as in the usual "isotropic" oscillator. The result (4) can also be obtained with quantum mechanics by making in (3) the substitution $M(n;\,n')=qA(0,\,1)$, and also $\nu(n,\,n')=-\nu$. Here $A(0,\,1)$ denotes the amplitude associated with a transition between the two lowest states of a one-dimensional oscillator. The theoretical value[63] of $|A(0,\,1)|^2$ is $h/8\pi^2m\nu$, showing that the vibrational term of the right side of (3) gives (4). The identity of results with the classical and quantum theories is not surprising, for complete agreement between the two theories is in general characteristic of the harmonic oscillator.[64] At visible wave-lengths, the impressed frequency ν_0 is so great compared to ν that the contribution of (4) to the total polarization is negligible compared to what it is with a constant field. Since such a field corresponds to zero impressed

[63] Cf., for instance, M. Born, "Problems of Atomic Dynamics," p. 84.

[64] We are apparently overlooking the fact that the axis of nuclear oscillation is continually rotating rather than stationary. However, we shall see classically in section 6 that the polarization of a harmonic oscillator is, at least in constant fields, unaffected by rotation of the molecule, (cf. also note 57) provided, of course, we neglect the slight distortion due to centrifugal expansion, and suppose that the nuclear rotation frequencies are negligible compared to those of vibration. A like result also holds in the quantum theory, as is to be expected since the spectroscopic stability relations given in part I show that summing over the discrete succession of quantized rotational motions gives the factor 1/3 due to spacial orientation quite as generally as the hypothesis of random orientations in the classical theory. The factor $M(n;\,n')$ in the vibrational part of the right-hand side of (3) must, in fact, have very approximately the same value as for a one-dimensional oscillator vibrating along a fixed axis, for otherwise a weak rotation would perceptibly change the total vibrational absorption, which is absurd. That a sufficiently slow rotation does not appreciably affect the validity of (4) in the quantum theory can also be seen explicitly by substituting the amplitude matrices for the rotating elastic dipole given by Mensing,[12] Oppenheimer,[13] or Fues,[13] and then adding the contributions of the "P" and "R" branches, which we have not resolved.

frequency, we see by (4) that the nuclear vibrations make a contribution $\alpha_{vib}=q^2/12\pi^2 m\nu^2$ to the constant α in the Debye formula (1) for the static dielectric constant. According to the suggestion of Debye or Ebert, we might expect that $4\pi N\alpha_{vib}=4\pi N\alpha-(n_0^2-1)$.

Measurements of the absolute intensity of infra-red vibrational absorption bands, which is proportional to the square of the oscillation in moment and hence to q^2, furnish estimates of the effective charge q, and show that the vibrational polarization calculated in the above paragraph is far too small to account for the observed discrepancy between the extrapolation of n^2 and the induced polarization part of the dielectric constant in HCl. The most accurate infra-red intensity measurements are probably those of Bourgin,[65] who finds that here $q=.828\times10^{-10}$ e.s.u. Introducing this value of q, and the values $m=1.62\times10^{-24}$, $\nu=8.82\times10^{13}$ of the effective mass and vibrational frequency of HCl in the preceding formula for α_{vib}, we find that $4\pi N\alpha_{vib}$ is only 1.5×10^{-6}, whereas we have seen that the discrepancy between n_0^2-1 and $4\pi N\alpha$ is 1.7×10^{-4}. Values of q have also been calculated by Dennison[66] for HBr, CO, CO_2, NH_3, CH_4 from various intensity measurements. These values are all less than one-fifth the electronic charge 4.774×10^{-10} and correspondingly $4\pi N\alpha_{vib}$ is of the order 10^{-6} and hence negligible, as in HCl. Of course, absolute intensities are hard to measure with precision,[67] and one wonders whether the experimental values of q may not be in error. However, to account for the discrepancy 1.7×10^{-4} in HCl the effective charge would have to be about 8.7×10^{-10} e.s.u. Since the absorption coefficient varies as q^2, the measurement of this coefficient would have to be in error by a factor about 100, which seems clearly out of the question inasmuch as Bourgin claims an error of only 10 or 20 percent.

Thus the absorption measurements apparently show very definitely that in molecules such as the hydrogen halides the vibrational polarization is too small to have any bearing on the discrepancy between refractive indices and dielectric constants. The possibility of electronic bands in the infra-red as an alternative explanation does not seem at all likely, for HCl is doubtless stable enough so that its lowest normal electronic absorption frequencies

[65] D. G. Bourgin, Phys. Rev., June, 1927. We use essentially Dennison's rather than Bourgin's definition of the effective charge, so that our q is dp/dr rather than p/r in Bourgin's notation. The reader must not confuse our q with the factor $k=\mu/r_0$ (Bourgin's q_0) by which we must multiply the nuclear separation to get the electrical moment when the molecule is at rest. It is, however, not unreasonable that q and k should be roughly of the same order of magnitude, and Bourgin's measurements seem to show that they are very nearly equal.

[66] D. M. Dennison, Phil. Mag. **1**, 195 (1926). Dennison used the old quantum theory but fortunately his amplitude for a harmonic oscillator agrees with the new mechanics, as does also Bourgin's half-quantum amplitude.

[67] As an instance of the error in absolute intensity measurements, the absorption coefficient calculated by Tolman and Badger (Phys. Rev. **27**, 383, 1926) from Czerny's intensity data on the pure rotation bands of HCl disagrees by a factor about 20 with the much more reliable theoretical value computed with the aid of the moment 1.03×10^{-18} demanded by the new quantum mechanics and Zahn's dielectric constant data (cf. Kronig[16]). The error in measuring the intensity of vibrational bands is presumably not as great, though we may note that Dennison's[66] value $.33\times10^{-10}$ of the effective charge q for HCl deduced from Bahr's and Burmeister's intensity data yields an absorption coefficient only 1/6 that of Bourgin's.

are in the ultra-violet. This, however, does not necessarily mean that in other kinds of molecules than HCl (e.g., perhaps ethyl-ether) there may not be infra-red vibrational or electronic bands of such large amplitude, high effective charge or low frequency as to have an important influence on the correlation of refractive indices and dielectric constants. It may be noted that in molecules such as HCl, the discrepancy between n_0^2-1 and $4\pi N\alpha$ is only a fraction of $4\pi N\alpha$, and that $4\pi N\alpha$ itself is often small compared to $\epsilon-1$. Therefore a small experimental error in the electrical moment, i.e., in the determination of the temperature coefficient of $(\epsilon-1)/N$ will suffice to explain away the discrepancy between n_0^2-1 and $4\pi N\alpha$. Thus in HCl, if we assume the absolute value of the total dielectric constant to be approximately correct, an increase [68] in the moment from Zahn's value 1.034×10^{-18} to 1.07×10^{-18} c.g.s.u., which corresponds to an error of 7 percent in the temperature coefficient of $(\epsilon-1)/N$, will increase the contribution of the permanent dipoles to the right-hand side of (1) enough so that the remainder $4\pi N\alpha$ is decreased to a value $.871\times10^{-3}$ in accord with optical data. An error of 5 percent in the absolute magnitude of the polarization would also account for the discrepancy. In ammonia the contribution of permanent dipoles to the dielectric constants so overshadows the induced polarization that in increase of only .3 percent in the moment, a change clearly within the experimental error, will diminish Zahn's[69] value .000768 for $4\pi N\alpha$ to a value .000729 in accord with the Cuthbertson[61] dispersion data. In ethyl-ether, on the other hand, the contribution of permanent dipoles is relatively small,[70] and the discrepancy thus much more vital. Doubtless future experimental refinements will minimize the discrepancy between optical and dielectric constant data in many instances. Zahn's recent work,[69] for instance, greatly improved the situation in ammonia. Also we shall see in the next section that the correction for the slight departures from the Debye formula in the quantum theory helps matters a little in some cases.

5. Limit of Accuracy of the Debye Formula in the Quantum Mechanics

In Part I we assumed that the nuclear rotation frequencies were smal compared to kT/h, so that we could develop the polarization as a power series in the ratio $s=h\nu(njm;nj'm')/kT$. In fact we disregarded terms beyond s^2 in the bracketed part of Eq. (9), part I. We have already mentioned on p. 34 that s is not small compared to unity for states with sufficiently large

[68] Against the possibility of an error in the moment of HCl may be mentioned the fact that Raman and Krishman (Phil. Mag. **3**, 713, 1927) deduce by an entirely different method involving combination of measurements on depolarization of light and the Kerr effect, a moment 1.04×10^{-18} in excellent accord with Zahn's value 1.03×10^{-18}. However, Raman and Krishman also similarly deduce a moment 1.66×10^{-18} for CH^3Cl, which does not agree at all with Sanger's[8] value 1.97×10^{-18} deduced from dielectric constants, of which they were not aware, and this suggests that the error in determining moments by one of the methods has been underestimated.

[69] C. T. Zahn, Phys. Rev. **27**, 455 (1926).

[70] Cf. Debye, Handbuch der Radiologie, vol. VI, p. 625.

rotational quantum numbers. We saw qualitatively in note 26 of part I, that the resulting error is not large because such states are relatively infrequent, and we shall now make a quantitative computation of this error by including two higher powers of s than previously. For explanation of the rather involved notation the reader is referred to part I. If we disregard terms beginning with s^5 instead of with s^3 in the bracketed factor of (9), part I, it is readily seen by using the same reasoning as in deducing Eq. (11), part I, that we must add to Eq. (1) the correction term

$$-(h^2B/12k^3T^3)\sum_{j,m,j',m'}\nu(njm\ ;\ nj'm')^2\,|\mu_z(jm\ ;\ j'm')\,|^2e^{-W(nj)/kT} \qquad (5)$$

The expression (5) is readily evaluated at high temperatures by comparison with the kinetic energy function. Let us assume the most general rigid[71] polyatomic molecule, having as a rule three unequal moments of inertia. There are then three degrees of rotational freedom, and the index j represents two quantum numbers, the third being denoted by m (cf. p. 733, part I). Let x_i, y_i, z_i be the coordinates of the ith constituent nucleus referred to a set of axes fixed in space, and let u_i, v_i, w_i be its coordinates referred to the principal axes of inertia, which rotate with the molecule. The center of gravity is, of course, to be chosen as the origin of both coordinate systems, and the electric field F is assumed to be applied along the z-axis. Since the molecule is rigid the coordinates u_i, v_i, w_i are constants("c-numbers") whereas $\mathbf{x}_i$, $\mathbf{y}_i$, $\mathbf{z}_i$ are matrices, and a typical element of $\mathbf{z}_i$ may be denoted[72] by $z_i(jm\,;j'm')$. By the rules for matrix multiplication the rotational kinetic energy of the state n, j, m is

$$\begin{aligned} T(njm) = \sum_i \{ 2\pi^2 m_i \sum_{j',m'} \nu(njm\ ;\ nj'm')^2\,|z_i(jm\ ;\ j'm')\,|^2 \} \\ +\ \text{similar terms in } x \text{ and } y, \end{aligned} \qquad (6)$$

where the summation over i includes all the nuclei in the molecule, as we may neglect the contributions of the electrons to the rotational energy. Now let I^u, I^v, I^w be unit vectors coinciding with the u, v, w axes respectively, and let $l_z{}^u(jm\,;j'm')$ denote a matrix element of the z-components of I^u, etc. Then

$$z_i(jm\ ;\ j'm') = u_i l_z{}^u(jm\ ;\ j'm') + v_i l_z{}^v(jm\ ;\ j'm') + w_i l_z{}^w(jm\ ;\ j'm') \qquad (7)$$

If we substitute (7), and the analogous formulas for x and y into (6), a considerable simplification ensues since "products of inertia" such as $\sum_i m_i u_i v_i$ vanish. Also $\sum m_i u_i{}^2$ is the moment of inertia U with respect to the plane vw, with corresponding definitions for V and W (this W must not be confused with an energy element $W(njm)$). The mean rotational energy is obtained by averaging over the various states j, m weighted according to the Boltzmann factor (cf. p. 733, part I). Consequently, using (7), and averaging, we find

[71] It is to be noted that we are now assuming a rigid molecule, whereas in Part I we made the perhaps less stringent requirement of a permanent dipole moment. The difference is unimportant here, as we are calculating only a correction term.

[72] We for brevity write the arguments of an element of z_i, etc., as $(jm;j'm')$ rather than as $(njm;nj'm')$ for the rigidity implies that there are no elements in which $n' \neq n$, making the index n unnecessary.

$$T_{\text{mean}} = 6\pi^2 BN^{-1} \sum_{j,m,j',m'} Uv(njm\ ;\ nj'm')^2 \,|l_z^u(jm\ ;\ j'm')\,|^2 e^{-W(nj)/kT} \qquad (8)$$
$$+ \text{ similar terms in } v \text{ and } w,$$

where B is defined as in Eq. (6), part I, and where, as on p. 736, we neglect the difference between $W(njm)$ and $W(nj)$. Instead of adding in the contributions of the x and y components in (8), we have multiplied by the factor 3, which is legitimate in view of the spectroscopic stability relations given in section 4, part I. Now the first line of (8) is the part of the mean kinetic energy resulting from the moment of inertia U with respect to the plane vw. This energy results partly from rotation about the v axis and partly from rotation about the w axis. It is, in fact, $UT_v/B + UT_w/C$, where T_v is the mean kinetic energy of rotation about the v axis, etc., and where A, B, C are the moments of inertia about the axes u, v, w respectively. This result follows inasmuch as $C = U + V$, so that a fraction U/C of T_w is due to U, etc. Here the reader must distinguish carefully between moments of inertia about *axes* and *planes* (denoted respectively by A, B, C and U, V, W) and also between the corresponding apportionments of energy. Now at ordinary temperatures the rotational energy can be calculated fairly accurately in most gases by the classical theorem of equipartition. This is evidenced by specific heats, and is due to the asymptotic connection of classical and quantum statistics for large quantum numbers. According to classical statistics the total rotational kinetic energy is $3kT/2$, and is apportioned equally between the three principal axes[73] (though not between the three principal planes). Therefore $T_u = T_v = T_w = \frac{1}{2}kT$ and hence the first line of (8) equals

$$\tfrac{1}{2}kT(U/B + U/C) \qquad (9)$$

with analogous results for the v and w parts of (8).

Now if the electrical moment vector is "permanent" and rigidly mounted on the molecules, its components μ_u, μ_v, μ_w along the u, v, w axes will be constants (c-numbers in Dirac's terminology) and $\mu_z(jm\,;j'm')$ will be given by a formula identical with the right side of (7) except that μ_u, μ_v, μ_w replace u_i, v_i, w_i. From this it follows that

$$\sum_{m,j'm'} |\mu_z(jm\ ;\ j'm')\,|^2 = \sum_{q=u,v,w} \Big\{ \sum_{m,j',m'} \mu_q{}^2 \,|l^q{}_z(jm\ ;\ j'm')\,|^2 \Big\} \qquad (10)$$

since sums of the form $\sum_{m,j',m'} l_z^u(jm\,;j'm') l_z^{v*}(jm\,;j'm')$ (*=conjugate) vanish because $\boldsymbol{l}^u$ and $\boldsymbol{l}^v$ are perpendicular vectors.[74] By (10) we see that the

[73] The proposition that classically the mean kinetic energy associated with each principal axis is $\frac{1}{2}kT$ is easily established by a simple change of variables in the integrals associated with the distribution function. In place of the three canonical momenta conjugate to the Eulerian angles we introduce "momentoids" proportional to the instantaneous angular velocities about the three principal axes. The kinetic energy then becomes the sum of three terms which are each proportional to the square of a momentoid and which represent respectively the kinetic energy about the three principal axes. The terms are then of the squared form to which the equipartition theorem can be applied separately. Cf. Jeans, Dynamical Theory of Gases, 3rd ed., p. 97, and footnote, p. 98.

[74] The vanishing of sums of this form is fairly obvious from the fact that it is the quantum analog of the fact that an expression of the form $\mathbf{a}_z\mathbf{b}_z$ vanishes on averaging over random orientations if $\mathbf{a}$ and $\mathbf{b}$ are perpendicular vectors. A more rigorous proof can be obtained by a slight extension of the spectroscopic stability argument given in Part I. A simple symmetry

contribution of μ_u to (5) differs from the first line of (8), and hence from (9), only by a factor $-N\mu_u^2h^2/72\pi^2Uk^3T^3$. Analogous results hold for the v and w contributions. Adding the correction term (5), thus evaluated, to the right side of (1), we obtain the revised Debye formula

$$\frac{3}{4\pi}\frac{\epsilon-1}{\epsilon+2}=N\alpha+\frac{N\mu^2}{3kT}[1-f(T)] \tag{11}$$

where the new feature in the correction term

$$f(T)=\frac{h^2}{48\pi^2kT\mu^2}\left[\mu_u^2\left(\frac{1}{B}+\frac{1}{C}\right)+\mu_v^2\left(\frac{1}{C}+\frac{1}{A}\right)+\mu_w^2\left(\frac{1}{A}+\frac{1}{B}\right)\right] \tag{12}$$

Thus in making the hypothesis of "slowness of precession" we simply disregarded higher powers of T in the denominator. If we had retained even higher powers of s, we would find $f(T)$ contained terms in T^{-2}, T^{-3}, etc. In the special case of diatomic molecules (case a or b, section 2), and of symmetrical polyatomic molecules (case c) we may take $\mu_w=\mu$, $\mu_v=\mu_u=0$, $A=B$, and then (12) becomes $f(T)=h^2/24\pi^2AkT$, the same value as previously obtained by Kronig[16] and Manneback[23] for cases (a) and (c) respectively by a quite different method. As noted by various writers, the correction term is usually small except at very low temperatures. In HCl, for instance, $f(T)$ is about .016 at ordinary temperatures. The main value of calculating (12) is to determine the limit of accuracy of the unmodified Debye formula in the quantum mechanics. In the classical theory, which corresponds to $h=0$, the correction of the type under consideration disappears completely.

The slight numerical correction due to $f(T)$ is, however, of some interest in correlating refractive indices and dielectric sonstants, for we have seen in section 4 that a slight change in the constants may materially alter the discrepancy between optical and electrostatic data. Experimentally the moment is approximately determined by the temperature coefficient of $(\epsilon-1)/N$ at a room temperature T_0, and hence with the correction μ^2 must be increased by a factor about $1+2f(T_0)$ to give this coefficient the same value as previously. Thus very roughly the effect of the correction is to increase the contribution of permanent dipoles to the susceptibility by a factor $1+f(T_0)$ and hence to diminish $N\alpha$ by an amount $N\mu^2f(T_0)/3kT_0$. A more careful calculation shows that Zahn's data for HCl can now be fitted as well with $\mu=1.06\times10^{-18}$, $4\pi N\alpha=.00098$ as before with his values 1.03×10^{-18} and .00104 respectively. Dispersion measurements give $n_0^2-1=.000871$, and thus the correction removes about one-third of the discrepancy between n_0^2-1 and $4\pi N\alpha$ in HCl, and decreases correspondingly the estimate made in section 4 of the experimental error necessary to explain the discrepancy.

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argument, however, shows most readily that such sums must vanish, for if they did not, the susceptibility would contain a term proportional to $\mu_u\mu_v$; alteration of the sign of μ_u would then change the susceptibility which is absurd since in our problem there is no criterion for distinguishing between the positive and negative u directions.

6. Classical Derivation of the Langevin-Debye Formula

In the present section we shall derive the Langevin or Debye formula by means of classical theory. Our proof will be roughly the classical analog of the quantum calculation given in part I, and is likewise more general than the ordinary demonstrations, though very easy for those understanding the use of angle and action variables.[75] Let us suppose that we have a multiply periodic dynamical system with f degrees of freedom, specified by $2f$ canonical variables $w_1^0, \cdots, w_f^0, J_1^0, \cdots, J_f^0$. We suppose further that the w^0's and J^0's are respectively true angle and action variables for the system in the absence of the field F. When $F=0$ the w^0's are thus linear functions $w_k=\nu_k t+\epsilon_k$ of the time t, while then the J^0's are constants which incidentally in the old quantum theory would be equated to integral multiples of h. Instead of being a matrix as in part I, the z-component of electrical moment will be a multiple Fourier series

$$M_z=\sum_\tau M_\tau^{(z)} e^{2\pi i(\tau w^0)}. \tag{13}$$

We use the same notation as in Born's "Atommechanik" (p. 86, etc.) Thus (τw^0) is an abbreviation for the expression $\tau_1 w_1^0+\cdots+\tau_f w_f^0$, and the subscript $\tau_1\,\tau_2\cdots\tau_f$ is abbreviated to τ. The summation is f-fold, and extends over all positive and negative values of the integers $\tau_1\cdots\tau_f$. The complex amplitudes $M_\tau^{(z)}$ are, of course, functions of the J^0's as well as the τ's, and $M_{-\tau}^{(z)}$ is the conjugate of $M_\tau^{(z)}$. Classical statistics show that if a field is applied along the z-direction, the susceptibility is

$$\chi=\frac{N\int\cdots\int M_z e^{-W(F)/kT}dJ^0dw^0}{F\int\cdots\int e^{-W(F)/kT}dJ^0dw^0}, \tag{14}$$

where we denote by dJ^0dw^0 an element of volume $dJ_1^0\cdots dJ_f^0dw_1^0\cdots dw_f^0$ of the "phase space" and the integral sign thus denotes f integrations. The integration, of course, corresponds classically to summation over a discrete series of allowed states in quantum mechanics. It is clearly to be understood that we are keeping the *original* canonical variables $w_1^0, \cdots, w_f^0, J_1^0, \cdots, J_f^0$. Since the transformation from a Cartesian to the w^0, J^0 system is thus not modified to take account of the field F, the w^0's and J^0's will cease to be true angle and action variables; i.e., cease to be respectively linear in t and constant, after the field F is applied. The w^0's and J^0's will, however, remain canonically conjugate, and we can apply (14) because it is a fundamental theorem in statistical mechanics that the a-priori probability is proportional to the volume occupied in the phase space, regardless of what $2f$ variables we choose as constituting the coordinates of this space

[75] For further detail on the dynamical technique underlying the use of angle and action variables, with which we assume some familiarity, see Born's "Atommechanik," or Chap. XI of the writer's "Quantum Principles and Line Spectra."

provided only they are canonical.[76] In (14) $W(F)$ denotes the energy or Hamiltonian function *in* the field F, and equals $W_0 - FM_z$, where M_z is given by (13), and W_0 is the energy function for $F=0$. W_0 is a function only of the J^0's whereas $W(F)$ involves also the w^0's through M_z. Now approximately $e^{-W(F)/kT} = e^{-W_0/kT}(1 + FM_z/kT + \cdots)$ and hence if we keep only the part of the susceptibility which is independent of F, Eq. (14) becomes

$$\chi = \frac{N \int\int M_z^2 e^{-W_0/kT} dJ^0 dw^0}{kT \int\int e^{-W_0/kT} dJ^0 dw^0} . \tag{15}$$

Here we have assumed that the polarization vanishes when $F=0$; i.e., that the numerator of (14) vanishes when $W(F)$ is replaced by W_0. An analogous assumption was made in supposing the first line of Eq. (5), part I, equaled zero, and a more detailed justification for the assumption is given on p.735, part I. Now since the square of two multiple Fourier series is itself such a series, M_z^2 may be expressed as a multiple Fourier series in the w^0's. On integrating over the w^0-part of the phase space the contributions of all terms in this multiple Fourier development of M_z^2 vanish except the constant term $(M_z^2)_0$, for integrals of periodic terms in the w^0's taken over a period[77] are zero. By the rules for multiplying together Fourier series term by term, (M_z^2) equals $\sum_\tau M_\tau^{(z)} M_{-\tau}^{(z)}$ which is, of course, a function only of the J^0's. Eq. (15) now becomes

[76] Another way of saying the same thing is that contact transformations have unit functional determinants, so that the "extension in phase" is invariant of the choice of canonical coordinates. Cf., for instance, Adams, "The Quantum Theory," 2nd ed., p. 26 (Bull. Nat. Research. Coun., No. 39).

[77] *Limits of integration in* (14)–(15). If we integrated over the entire phase space in the J^0, w^0 system the limits of integration for each of the w^0's in (14) or (15) would be from $-\infty$ to $+\infty$, as all of the w^0's may increase without limit. However, since the system is cyclic in each of the w^0's with unit period, it is clear that we will obtain the correct statistical average if we take the limits of integration for each of the w^0's as zero and unity. Another way of saying the same thing is that Cartesian variables are multiple valued in the w^0's, so that the entire Cartesian phase space corresponds to only one period for the w^0's.

The limits of integration for the J^0's can usually be taken as 0 and $+\infty$ by proper choice of the fundamental periods. (The limits, however, are $-\infty$ and $+\infty$ for J^0's associated with both left and right-handed rotations, as, for instance, the J^0 associated with the axial component of angular momentum.) The system must, of course, be of the type for which the J^0-integrals converge; i.e., be of a kind for which classical statistical mechanics have a meaning. This ordinarily means that the energy ranges from some finite value to $+\infty$. This condition is not met in any actual Rutherford atom based on the inverse square law, for there the energy ranges from $-\infty$ to 0, and the writer has already remarked elsewhere (cf. "Quantum Principles and Line Spectra," p. 14) that purely classical statistics are meaningless as applied to an actual atomic system, for they would give an overwhelming probability that the electrons be infinitely close to the nucleus. The only way of avoiding this difficulty would be to employ a rather illogical "semi-classical" theory in which we apply classical statistics to the degrees of freedom for which the J^0-integrals converge, but confine the remaining J^0's to certain particular (i.e., in a sense "quantized") values.

$$\chi = \frac{N\int (M_z^2)_0 e^{-W_0/kT} dJ^0}{kT\int e^{-W_0/kT} dJ^0} = \frac{N\overline{M^2}_z}{kT},$$

where $\overline{M_z}^2$ denotes the statistical mean square of M_z in the absence of the field F; i.e. the average over the J^0-space, weighted according to the Boltzmann factor, of the time average value of M_z^2 for an orbit having given values of the J^0's. Now if there are no external fields present when $F=0$, or, if as is usually the case, the other fields are weak enough so that we may neglect their effect on the spacial distribution, it is clear that all spacial orientations will be equally probable, and the mean squares of the x, y, and z components of moment will be equal. We may then replace $\overline{M_z}^2$ by one-third the statistical mean square of the vector moment $\boldsymbol{M}$ of the molecule. Thus we have

$$\chi = N\overline{\boldsymbol{M}^2}/3kT, \tag{16}$$

which is a sort of generalized Langevin or Debye formula.

Our derivation of (16) is considerably shorter than the quantum proof of the Langevin-Debye formula given in Part I. The reason for this is that we are able to apply classical statistical theory keeping the same set w^0, J^0 of canonical variables as in the absence of F, even though these variables undergo perturbations. Since $dw^0 dJ^0 = dw dJ$, Eq. (16) might also be deduced by starting with a formula identical with (14) except that the variables of integration are $w_1, \cdots, w_f, J_1, \cdots, J_f$ instead of $w_1^0, \cdots, w_f^0, J_1^0, \cdots, J_f^0$. Here the w's and J's (in distinction from the w^0's and J^0's) denote a set of true angle and action variables for the perturbed system, which are respectively linear in t and constant even when F does not vanish, and which are deduced from Cartesian variables by a transformation involving F. Then $W(F)$ is a function only of the J's, viz., $W(F) = W_0 - F(M_z^{(F)})_0$, and the effect of integrating over the w's is simply to replace the integrand M_z by the constant term $(M_z^{(F)})_0$ of its multiple Fourier development in the w's. Here $(M_z^{(F)})_0$ is not the same as the constant term $M_0^{(z)}$ of the development (13) in the w^0's and perturbation theory shows that

$$(M_z^{(F)})_0 = M_0^{(z)} - 2F\Sigma_{(\tau\nu^0)>0}\Sigma_k \tau_k \frac{\partial}{\partial J_k}\left(\frac{|M_\tau^{(z)}|^2}{(\tau\nu^0)}\right), \tag{17}$$

where the arguments of $M_0^{(z)}$ and the $M_\tau^{(z)}$ are to be taken as the J's rather than J^0's. Eq. (17) is the classical analog of Eq. (3), Part I. For proof of (17) see, for instance, Born, Zeits. f. Physik, **26**, 385 (1924); Eq. (17) is the extrapolation of Eqs. (22) and (24) of his article to infinitely long impressed wave-lengths.

The proof by the w, J method outlined in the preceding paragraph parallels in a much closer and more illuminating fashion the quantum calculation given in Part I than does the w^0, J^0 method. We have nevertheless given the w^0, J^0 method in detail because it is the simpler. If we use instead the w's and J's it is necessary to integrate by parts to get rid of the J-derivatives in (17). This partial integration corresponds in a general way to the manipulation used in simplifying Eq. (5) into (11) in Part I.

Eq. (16) does not appear to have previously been given in its full generality, and is much more comprehensive than the ordinary Eq. (1), since the statistical mean square moment appearing in (16) must not be confused with the time average for an individual orbit or atom, and is in general a function of the temperature. Eq. (16) reduces to (1) only with certain simplying assumptions.

Rigid model. If we assume that the molecule has a permanent moment μ independent of the J's then we may replace $\overline{M^2}$ by μ^2 in (16). The present method thus shows that the contribution of the permanent dipoles to the susceptibility is given by the familiar Langevin expression $N\mu^2/3kT$ even in the most asymmetrical rigid molecules, despite the kinetic energy of rotation. Such a molecule has, of course, three unequal moments of inertia and three rotational degrees of freedom corresponding to three pairs of action and angle variables.

Elastic model. In general the molecule is elastic, so that the moment vector $\boldsymbol{M}$ vibrates about its mean value, and we shall show that this effect is responsible for the induced polarization, or first right-hand term of Eq. (1). Let us assume the molecule has $p=f-3$ vibrational degrees of freedom associated with oscillations about an equilibrium configuration in addition to the three rotational degrees of freedom. This model cannot be regarded as corresponding to physical reality, for in actual Rutherford atoms the electrons do not have positions of static equilibrium, although the nuclei do approximately. This objection, however, need not alarm us, for we have already mentioned in note 77 that classical statistics cannot be applied to a real atom or molecule, and it is only by picturing the electrons as linear oscillators that pure classical theory can explain dispersion, etc. Let the p vibrations have frequencies ν_i, effective charges q_i, and effective masses $m_i (i=1, \cdots, p)$. We shall suppose the vibrations small enough so that the restoring forces can be regarded as linear, and neglect the slight distortion of the vibration frequencies, etc., by centrifugal force caused by rotation of the molecule as a whole. Then the vector moment $\boldsymbol{M}$ will be the sum of a constant term $\boldsymbol{M}_0$ and p terms $\boldsymbol{M}_1$, $\boldsymbol{M}_2$, $\cdots$ which are simple harmonic functions of the time with frequencies ν_1, ν_2, $\cdots$ respectively, and on the average M^2 equals $M_0^2+M_1^2+M_2^2+\cdots$. This separation of $\boldsymbol{M}$ into $\boldsymbol{M}_0$ and periodic terms corresponds roughly to the resolution of the moment matrix into low and high frequency elements in part I. Furthermore $\boldsymbol{M}_1$ differs from the vector amplitude $\boldsymbol{A}_1$ of the corresponding oscillation only by a factor q_1, and therefore $\overline{M_1^2}$ equals $kTq_1^2/4\pi^2 m_1\nu_1^2$, etc., since the mean of the kinetic energy $2\pi^2\nu_1^2 m_1 A_1^2$ of a harmonic oscillator with one degree of freedom is $\frac{1}{2}kT$. Thus the mean square of the vibrational moment is proportional to T, and this cancels the T in the denominator of (16), so that the contribution of the p vibrations to the susceptibility is an expression

$$N\alpha = N\sum_{i=1,\ldots,p} q_i^2/12\pi^2 m_i\nu_i^2$$

which is independent of the temperature at constant density. In case the vibrations are due entirely to one isotropic oscillator per molecule, then as such an oscillator represents three degrees of freedom, we have $p=3$ and ν, m, q are independent of the index i, so that the formula[78] for $N\alpha$ reduces

[78] Because all three vibrational degrees of freedom have the same frequency the time average of "cross-terms" such as $\mathbf{M}_i\mathbf{M}_j$ will not vanish for an individual molecule, and so at first thought it might appear as though we were not justified in assuming above that the statistical mean of $\mathbf{M}^2$ is the same as that of $\mathbf{M}_0^2+\mathbf{M}_1^2+\mathbf{M}_2^2+\cdots$. The "cross-terms," however, vanish when we integrate over the w^0 part of the phase space, which is tantamount to averaging over all possible phase relations between the different degrees of freedom.

to $Nq^2/4\pi^2 m\nu^2$. This result could also be obtained in a well known elementary way if we assumed static equilibrium and simply equated the linear restoring force to the polarizing force Fq, and our treatment of the polarization of an isotropic oscillator as a special case of (16) is quite a contrast to the usual elementary method, but the latter has, of course, the objection that it does not consider the effect of either rotational or kinetic energy.[79]

Correction for centrifugal expansion. In the model used in the preceding paragraph the magnitude of the constant part $\boldsymbol{M}_0$ of the vector moment will be nearly the same for all molecules, and hence independent of the J^0's, so that very approximately we may take $\overline{M_0}^2=\mu^2$, thus yielding the second right-hand term of (1). We have, however, already mentioned in part I, that there is a slight correction for centrifugal expansion. We may now compute this quantitatively for an actual diatomic molecule in which the vibrations are due to nuclear oscillations along the axis of the molecule. The model representing the nuclear motions thus has one degree of vibrational freedom and is not to be confused with the isotropic oscillator studied at the end of the preceding paragraph. Let r_0, I, and μ be respectively the nuclear separation, moment of inertia, and (scalar) moment when the molecule is at rest. Then if the molecule rotates with an angular velocity ω we find on equating the centrifugal force $mr\omega^2$ to the restoring force $4\pi^2\nu^2 m(r-r_0)$ that the nuclear separation increases by an amount $r-r_0=r_0\omega^2/4\pi^2\nu^2$ if $r-r_0$ is small. The corresponding increase in electrical moment is $q(r-r_0)$. Here the effective mass m, effective charge q, and frequency ν are defined as on p. 44. Consequently we have approximately

$$\overline{M_0}^2=\mu^2+2\mu q(\bar{r}-r_0)=\mu^2+\mu q r_0\overline{\omega^2}/2\pi^2\nu^2 \quad \text{or} \quad \overline{M_0}^2=\mu^2+\mu q r_0 kT/I\pi^2\nu^2$$

since the mean rotational kinetic energy $\frac{1}{2}I\overline{\omega^2}$ is kT. The effect of centrifugal expansion is thus only a contribution $\mu q r_0/3\pi^2 I\nu^2$ to the constant α in Eq. (1). This contribution is, however, usually quite negligible. In HCl, for instance, it accounts for less than one percent of α with Bourgin's value of q. The same formula for the correction due to centrifugal expansion can also be obtained with quantum mechanics, using the amplitude matrices for the elastic rotating dipole given by Miss Mensing,[12] Oppenheimer,[13] or Fues.[13] The agreement of quantum and classical methods in this instance is, of course, simply because rotational frequencies are usually small compared to kT/h. On the other hand, the correction for non-linearity in the polarization due to an oscillator would be entirely different calculated by (16) and by quantum mechanics, for quanta of vibratory energy are usually large compared to kT.

The writer wishes to thank Prof. Debye for the opportunity of discussing with him the manuscript of the present paper.

Department of Physics,
University of Minnesota,
May 5, 1927.

[79] Prof. Debye in his Madison lectures also derives Eq. (1) for this model of harmonic oscillators mounted on a rotating molecule. His method is somewhat different, as he integrates with momentoids such as were mentioned in note 73 rather than with angle and action variables. He proves the influence of vibrational kinetic energy inconsequential also in Handbuch der Radiologie, vol. VI, p. 613.

A MODIFICATION OF GORDON'S EQUATIONS

By H. Bateman

Abstract

The expressions for the density of electricity and current given recently by W. Gordon are modified so as to give the wave-equations used by de Broglie and Schroedinger. The new equations are derived from a variational principle which also gives some other equations of considerable interest. A stress-energy tensor is derived from the Lagrangian function by Schroedinger's rule and is used to determine one of the constants in Schroedinger's equation. The analysis seems to indicate that a stationary, isolated electron has a definite boundary and uniform volume density of electricity.

I. Derivation of the Field and Wave-Equations from a Variational Principle

Let us consider a Lagrangian function L which is the sum of four terms

$$L=L_1+L_2+L_3+L_4$$

where

$$L_1=\tfrac{1}{2}(e^2-h^2)$$

$$L_2=(\rho/c)\left[(v\cdot a)-c\phi+(v\cdot A)-c\Phi\right]$$

$$L_3=\frac{1}{c^2}\frac{\partial\psi}{\partial t}\frac{\partial\bar{\psi}}{\partial t}-\frac{\partial\psi}{\partial x}\frac{\partial\bar{\psi}}{\partial x}-\frac{\partial\psi}{\partial y}\frac{\partial\bar{\psi}}{\partial y}-\frac{\partial\psi}{\partial z}\frac{\partial\bar{\psi}}{\partial z}-k^2\psi\bar{\psi}$$

$$+l^2\psi\bar{\psi}\left[\Phi^2-A_x^2-A_y^2-A_z^2\right]$$

$$-il\left[A_x\left(\psi\frac{\partial\bar{\psi}}{\partial x}-\bar{\psi}\frac{\partial\psi}{\partial x}\right)+A_y\left(\psi\frac{\partial\bar{\psi}}{\partial y}-\bar{\psi}\frac{\partial\psi}{\partial y}\right)\right.$$

$$\left.+A_z\left(\psi\frac{\partial\bar{\psi}}{\partial z}-\bar{\psi}\frac{\partial\psi}{\partial z}\right)+\frac{1}{c}\Phi\left(\psi\frac{\partial\bar{\psi}}{\partial t}-\bar{\psi}\frac{\partial\psi}{\partial t}\right)\right]$$

$$L_4=\theta\rho(1-v^2/c^2)^{1/2}+\frac{1}{2}\left[\frac{1}{c^2}\left(\frac{\partial\theta}{\partial t}\right)^2-\left(\frac{\partial\theta}{\partial x}\right)^2-\left(\frac{\partial\theta}{\partial y}\right)^2-\left(\frac{\partial\theta}{\partial z}\right)^2\right]$$

We shall make

$$\delta\int\int\int\int L\,dx\,dy\,dz\,dt=0$$

on the supposition that ϕ, a_x, a_y, a_z, Φ, A_x, A_y, A_z, ρ, ρv_x, ρv_y, ρv_z, ψ, $\bar{\psi}$, and θ are to be varied independently[1] and that

$$\boldsymbol{h}=\operatorname{curl}\boldsymbol{a}, \qquad \boldsymbol{e}=-(1/c)\partial a/\partial t-\nabla\phi \tag{1}$$

We shall regard $(\boldsymbol{e}, \boldsymbol{h})$ as the field of the electron, $(\boldsymbol{a}, \phi)$ as the electromagnetic potentials of the electron's field, $(\boldsymbol{A}, \Phi)$ as the electromagnetic potentials of an external field which acts on the electron, ρ as the volume density of electricity belonging to the electron, v as the velocity of this electricity, ψ and $\bar{\psi}$ as conjugate complex quantities which will be found to satisfy equations analogous to Schroedinger's wave-equation and θ as a scalar potential of the type used in a previous paper. The field derived from $\boldsymbol{A}$ and Φ is supposed to be specified in the usual way by the equations

$$\boldsymbol{H}=\operatorname{curl}\boldsymbol{A}, \qquad \boldsymbol{E}=-(1/c)\partial\boldsymbol{A}/\partial t-\nabla\Phi \tag{2}$$

Varying a_x, a_y, a_z, and ϕ we obtain the usual field equations for the electron's field, viz.

$$\operatorname{curl}\boldsymbol{h}-(1/c)\partial\mathbf{e}/\partial t=\rho\boldsymbol{v}/c, \qquad \operatorname{div}\boldsymbol{e}=\rho \tag{3}$$

Varying ρ, ρv_x, ρv_y, ρv_z we obtain the equations

$$\beta\theta=\phi+\Phi$$
$$\beta\theta v_x/c=a_x+A_x, \qquad \beta=(1-v^2/c^2)^{-1/2} \tag{4}$$

Varying A_x, A_y, A_z and Φ we obtain the equations

$$\rho+\frac{il}{c}\left(\psi\frac{\partial\bar{\psi}}{\partial t}-\bar{\psi}\frac{\partial\psi}{\partial t}\right)-2l^2\psi\bar{\psi}\Phi=0$$
$$\frac{\rho v_x}{c}-il\left(\psi\frac{\partial\bar{\psi}}{\partial x}-\bar{\psi}\frac{\partial\psi}{\partial x}\right)-2l^2\psi\bar{\psi}A_x=0 \tag{5}$$
$$\cdots\cdots\cdots\cdots\cdots\cdots$$

which are very similar to those used by Gordon.[2]

Varying ψ and $\bar{\psi}$ independently we obtain the wave-equations

$$\Box\bar{\psi}=\bar{\psi}(k^2+l^2\Omega^2)+2il(A\bar{\psi})$$
$$\Box\psi=\psi(k^2+l^2\Omega^2)-2il(A\psi) \tag{6}$$

[1] We must also allow for the possibility that $\rho, \rho v, \psi$, and ψ may be discontinuous at certain surfaces but discontinuous in such a way that L is continuous. In the first draft of the paper the quantities ρ and ρv were not varied and equations (4) were not used. The present form of the theory seems preferable. The idea of varying ρ and ρv also was mentioned by me to Professor Lorentz as a possible answer to his remark that all the equations ought to be derivable from the variational principle whereas in the first form of the theory some of the equations were derived from the equations of conservation. Indeed it appears that with a stress-energy tensor derived by Schroedinger's rule the equations of conservation are satisfied identically only when all the quantities (other than constants) occurring in the Lagrangian function are varied. When some of the quantities are not varied the equations of conservation lead to a new set of equations supplementary to those derived from the variational principle.

[2] W. Gordon, Zeits. f. Physik **40**, 117 (1926).

in which

$$\Box\psi=\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}-\frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2}$$

$$(A\psi)=A_x\frac{\partial\psi}{\partial x}+A_y\frac{\partial\psi}{\partial y}+A_z\frac{\partial\psi}{\partial z}+\frac{1}{c}\Phi\frac{\partial\psi}{\partial t}$$

$$\Omega^2=A_x^2+A_y^2+A_z^2-\Phi^2$$

Finally varying θ we obtain the equation

$$\Box\theta+\rho(1-v^2/c^2)^{1/2}=0 \tag{7}$$

From the field equations we obtain the usual equation of continuity

$$\partial\rho/\partial t+\mathrm{div}(\rho v)=0 \tag{8}$$

With the aid of this equation and the wave-equations satisfied by ψ and $\bar{\psi}$ we may conclude from the expressions for ρ and ρv that if ψ and $\bar{\psi}$ are different from zero

$$\mathrm{div}\,\boldsymbol{A}+(1/c)\partial\Phi/\partial t=0 \tag{9}$$

If a corresponding equation holds for the external field of each electron and proton in the universe we may perhaps infer that we have also

$$\mathrm{div}\,\boldsymbol{a}+(1/c)\partial\phi/\partial t=0 \tag{10}$$

It is possible, moreover, that a theory of the present type may hold when an electromagnetic field is divided into two parts and then $(\boldsymbol{a}, \phi)$ can be regarded as the potentials of an external field and (10) will hold.

If this equation does hold, Eqs. (4) give the interesting equation

$$\partial(\beta\theta)/\partial t+\mathrm{div}\,(\beta\theta v)=0 \tag{11}$$

Combining this with the equation of continuity we find that

$$\frac{d}{dt}\left(\frac{\theta}{\rho(1-v^2/c^2)^{1/2}}\right)=0 \tag{12}$$

where

$$d/dt=\partial/\partial t+v_x\partial/\partial x+v_y\partial/\partial y+v_z\partial/\partial z \tag{13}$$

Equations (4) also give

$$\theta^2=(\phi+\Phi)^2-(a_x+A_x)^2-(a_y+A_y)^2-(a_z+A_z)^2$$

2. The Stress Energy Tensor

A stress-energy tensor satisfying the equations of conservation may be derived from the Lagrangian function by Schroedinger's rule.[3] Its components are of the types

[3] Schroedinger, Ann. d. Physik **82**, 265 (1927).

$$W=\frac{1}{2}(e^2+h^2)+\frac{2}{c^2}\frac{\partial\psi}{\partial t}\frac{\partial\bar{\psi}}{\partial t}+2l^2\psi\bar{\psi}\Phi^2$$

$$-\frac{2il}{c}\Phi\left(\psi\frac{\partial\bar{\psi}}{\partial t}-\bar{\psi}\frac{\partial\psi}{\partial t}\right)-2\rho(\phi+\Phi)+\frac{1}{c^2}\left(\frac{\partial\theta}{\partial t}\right)^2+\beta\rho\theta-L$$

$$X_x=e_x^2+h_x^2-\frac{1}{2}(e^2+h^2)-2\frac{\partial\psi}{\partial x}\frac{\partial\bar{\psi}}{\partial x}-2l^2\psi\bar{\psi}A_x^2$$

$$-2ilA_x\left(\psi\frac{\partial\bar{\psi}}{\partial x}-\bar{\psi}\frac{\partial\psi}{\partial x}\right)+\frac{2\rho v_x}{c}(a_x+A_x)-\left(\frac{\partial\theta}{\partial x}\right)^2-\beta\rho\theta\frac{v_x^2}{c^2}-L$$

$$X_y=e_xe_y+h_xh_y-\frac{\partial\psi}{\partial x}\frac{\partial\bar{\psi}}{\partial y}-\frac{\partial\psi}{\partial y}\frac{\partial\bar{\psi}}{\partial x}-2l^2\psi\bar{\psi}A_xA_y \tag{14}$$

$$-ilA_x\left(\psi\frac{\partial\bar{\psi}}{\partial y}-\bar{\psi}\frac{\partial\psi}{\partial y}\right)-ilA_y\left(\psi\frac{\partial\bar{\psi}}{\partial x}-\bar{\psi}\frac{\partial\psi}{\partial x}\right)$$

$$+\frac{\rho v_x}{c}(a_y+A_y)+\frac{\rho v_y}{c}(a_x+A_x)-\frac{\partial\theta}{\partial x}\frac{\partial\theta}{\partial y}-\beta\rho\theta\frac{v_xv_y}{c^2}=Y_z$$

$$S_x=c(e_yh_z-e_zh_y)-\frac{\partial\psi}{\partial x}\frac{\partial\bar{\psi}}{\partial t}-\frac{\partial\psi}{\partial t}\frac{\partial\bar{\psi}}{\partial x}+2l^2c\psi\bar{\psi}A_x\Phi$$

$$-ilA_x\left(\psi\frac{\partial\bar{\psi}}{dt}-\bar{\psi}\frac{\partial\psi}{\partial t}\right)-ilc\Phi\left(\psi\frac{\partial\psi}{dx}-\bar{\psi}\frac{\partial\psi}{\partial x}\right)$$

$$-\rho c(a_x+A_x)-\rho v_x(\phi+\Phi)-\frac{\partial\theta}{\partial x}\frac{\partial\theta}{\partial t}+\beta\rho\theta v_x=c^2G_x$$

In these equations W is the density of the energy, G that of the momentum, $X_x, X_y, \cdots$, are component stresses, S_x, S_y, S_z the components of a vector giving the flow of energy. The equations of conservation

$$\begin{aligned}&\partial X_x/\partial x+\partial X_y/\partial y+\partial X_z/\partial z-\partial G_x/\partial t=0\\&\partial S_x/\partial x+\partial S_y/\partial y+\partial S_z/\partial z+\partial W/\partial t=0\end{aligned} \tag{15}$$

are satisfied identically in virtue of the set of equations derived from the variational principle.

3. A Model of the Electron

To determine the constants l and k we consider the ideal case in which $A=\Phi=0$. The wave-equations are now

$$\Box\psi=k^2\psi, \qquad \Box\bar{\psi}=k^2\bar{\psi} \tag{16}$$

and are satisfied by

$$\psi = e^{ikct}(\sigma + \omega/r), \qquad \bar{\psi} = e^{-ikct}(\sigma + \omega/r)$$

where σ and ω are arbitrary constants. The supposition that σ and ω are different from zero at a great distance from the origin leads to an infinite amount of energy on account of the term $k^2\psi\bar{\psi}$ in W. To avoid this difficulty we assume

$\psi = \sigma e^{ikct}$,	$\bar{\psi} = \sigma e^{-ikct}$	inside the electron
$\psi = 0$,	$\bar{\psi} = 0$	outside the electron

To determine the constant σ we substitute in the equations

$$\begin{aligned} \rho &= (il/c)(\bar{\psi}\partial\psi/\partial t - \psi\partial\bar{\psi}/\partial t) \\ \rho v_z/c &= il(\psi\partial\bar{\psi}/\partial x - \bar{\psi}\partial\psi/\partial x) \end{aligned} \tag{17}$$

which imply that ρ is constant inside the electron and zero outside. They also give $v = 0$ so that in the present case the electron is stationary and the equations (4) now give $\theta = \phi$, $\boldsymbol{a} = 0$.

If $-\epsilon$ denotes the charge and V the volume of the electron our expression for ρ gives

$$\epsilon = 2k\sigma^2 Vl \tag{18}$$

The energy density is now given by

$$\begin{aligned} W &= 2\sigma^2k^2 - \rho\phi + (\partial\phi/\partial x)^2 + (\partial\phi/\partial y)^2 + (\partial\phi/\partial z)^2 && \text{inside the electron,} \\ &= (\partial\phi/\partial x)^2 + (\partial\phi/\partial y)^2 + (\partial\phi/\partial z)^2 && \text{outside the electron.} \end{aligned}$$

But by a well known theorem in electrostatics, the integral

$$\iiint [(\partial\phi/\partial x)^2 + (\partial\phi/\partial y)^2 + (\partial\phi/\partial z)^2]\, dx\, dy\, dz$$

over all space is equal to the integral

$$\iiint \rho\phi\, dx\, dy\, dz$$

taken over the electron, consequently the total energy is simply

$$\iiint 2\sigma^2k^2\, dx\, dy\, dz$$

taken over the electron and this is equal to $2\sigma^2k^2V = k\epsilon/l$. Equating this to mc^2 and giving the constant k the value

$$k = 2\pi mc/h$$

used by de Broglie, we obtain the equation

$$l=2\pi\epsilon/ch$$

This gives the value of one of the constants in the wave-equation or, if the value of this constant is supposed to be known it shows that the charge on the model electron is indeed $-\epsilon$.

It should be remarked that although ψ, $\bar{\psi}$ and ρ are discontinuous at the surface of the electron the stress across an element of the boundary is continuous. The Lagrangian function L is also continuous.

4. Discussion

The conclusion that an isolated electron has a sharp boundary may seem at first to be contrary to the leading ideas of the wave-theory of matter and perhaps the present theory may be wrong on that account. It is possible of course, that the sharp boundary may disappear when there is an external field. On the other hand a surface of discontinuity for ρ, ρv, ψ and $\bar{\psi}$ may still persist even if the electron's electricity extends over all space when there is an external field.

The existence of a surface of discontinuity may not be incompatible with the ideas of the wave theory of matter for the following reason. A function ψ which is expanded in a series of normal functions which are finite and continuous throughout space may very well represent a discontinuous function. In Schroedinger's theory of the Balmer lines of the hydrogen spectrum the essential point is that the normal functions are determined by the conditions of finiteness and continuity and it is to these normal functions that his original variational principle was applied.

In conclusion I wish to thank Professors Schroedinger and Lorentz for some useful comments and information.

California Institute of Technology,
March 30, 1927.

THE HALL EFFECT IN A BISMUTH CRYSTAL

By C. W. Heaps

Abstract

The Hall effect has been measured in plates cut in different directions from a single large crystal of bismuth. At room temperatures when the field H is perpendicular to the trigonal axis, a negative Hall coefficient R is obtained, decreasing from about 15 for $H=1000$ gauss to about 7 for $H=8000$. For H parallel to the trigonal axis a positive coefficient of about unity is obtained, increasing slightly with the field. At $-186°$C R is positive for all orientations of the axis and decreases as H increases. The maximum R observed at $-186°$C was $+15$ at $H=600$. A plate made of compressed bismuth powder gave $R=+7$, approximately, at $-186°$C. Beckman found large negative values of R for similar plates at this temperature. The Hall e.m.f. cannot be resolved into positive and negative components at $-186°$C in the way suggested by Becquerel.

THE Hall effect has been studied in bismuth crystals by several physicists. Van Everdingen[1] concludes that the (negative) Hall coefficient is large for a magnetic field perpendicular to the principal crystallographic axis and very small for a magnetic field parallel to the principal axis, while the coefficient for a magnetic force in any direction can be deduced from those in both principal cases with the aid of an ellipsoid of revolution. In his first report van Everdingen states that for the magnetic field parallel with the crystalline axis a negative coefficient is obtained in small magnetic fields and a positive coefficient in larger fields. Onnes and Beckman[2] later used van Everdingen's crystal and secured similar results.

When the bismuth crystal was cooled to low temperatures Onnes and Beckman found the Hall coefficient to be positive for all orientations of the axis and all field strengths. Becquerel,[3] on the other hand, found at the temperature of liquid air, a negative coefficient for small fields parallel to the principal crystallographic axis, and a positive coefficient for large fields. Lownds[4] has found that at low temperatures the Hall coefficient is positive when the field is perpendicular to the crystallographic axis.

These results with single crystals are not all in good agreement with each other. There is uncertainty regarding the existence of a positive Hall coefficient at room temperatures. Furthermore, the results at low temperatures are difficult to reconcile with each other. From the work of Onnes and Beckman on a single crystal at low temperatures it would appear that a specimen composed of crystal conglomerates of random orientation

[1] E. van Everdingen, Com. Phys. Lab. Leiden No. 61, 23 (1900).
[2] H. Kamerlingh Onnes and B. Beckman, Com. Phys. Lab. Leiden No. 129, No. 132 (1912).
[3] J. Becquerel, Comptes rendus **154**, 1795 (1912).
[4] L. Lownds, Ann. d. Physik **9**, 677 (1902).

should have a positive Hall coefficient. Experiments on plates of compressed bismuth powder, however, have given large negative coefficients.[5]

The writer has performed some experiments seeking to find the reason for the above-mentioned discrepancies.

Apparatus and Method

A single large bismuth crystal was made by very slowly cooling a molten mass of bismuth (listed as c. p. by Eimer and Amend) in a small electric furnace. When segments were split off from the edge of this specimen the plane of easy cleavage was found to extend completely and perfectly across the entire specimen. The normal to this cleavage plane is known to be the trigonal axis of the crystal.[6]

The working specimens were cut from this large crystal with considerable care, and electrical contacts were made by copper wires soldered with Wood's metal. A primary current of one ampere was used and the Hall e.m.f. was measured by the use of a galvanometer of sensitivity 11.4 mm per microvolt. A potentiometer in the galvanometer circuit was used for balancing the Hall e.m.f. Ebonite insulation was used throughout to insulate the primary and secondary circuits from earth, since imperfect insulation was found to introduce appreciable errors when a small effect was being measured.

The magnetic field was produced by an electromagnet with pole-pieces 1.05 cm apart and 5.6 cm in diameter. At liquid air temperatures a Weiss electromagnet with pole-pieces 3.7 cm apart and 10 cm in diameter was used.

Preliminary experiments showed quite a large dissymmetry in the Hall e.m.f. for the two directions of the magnetic field. However, when the Hall terminals were adjusted to be quite accurately on an equipotential surface in zero field this dissymmetry was made quite small. The existence of this phenomenon—which has been known for a long time[7]—does not appear to prevent accurate determinations of the Hall coefficient because the average e.m.f. when the dissymmetry was small was found to be practically the same as the average when the dissymmetry was large.

Thermomagnetic effects were found to be too large to ignore. They were allowed for as follows. With primary current flowing and the magnetic field acting, the potentiometer reading for balance was noted. The primary current was then broken and the potentiometer setting for balance was again immediately observed. The difference of the potentiometer settings gave the Hall e.m.f. To secure the potentiometer setting at the instant of breaking the primary current the following method was used. Switches were operated so that the galvanometer circuit was closed immediately after the primary current was broken. There was in general an immediate deflection of the galvanometer. By properly adjusting the potentiometer a setting could

[5] H. Kamerlingh Onnes and K. Hof, Com. Phys. Lab. Leiden No. 142 (1914).

[6] Bismuth crystallizes in the dihexagonal alternating class of the hexagonal system. The edges of the rhombohedron meet in the trigonal axis and the angle between any two of these edges is 87°34′. The cleavage plane is parallel to the (111) planes and is perpendicular to the trigonal axis.

[7] E. van Everdingen, Com. Phys. Lab. Leiden Sup. No. 2 (1901).

be secured such that the galvanometer experienced no deflecting force at the instant of closing the switch in the galvanometer circuit. This setting gave the e.m.f. to be subtracted from the e.m.f. observed when the primary current flowed. Such a procedure is satisfactory when the Hall terminals are initially accurately adjusted to lie on an equipotential surface.

Discussion of Results

The curves of Fig. 1 give the values of R, the Hall coefficient, as a function of the magnetic field H. The symbols $\parallel$ and $\perp$ after the designating letter on each curve indicate that the field was parallel or perpendicular, respectively, to the trigonal axis of the crystal.

Curves A and A' are for a plate of dimensions $0.99\times0.347\times0.058$ cm, cut with its length perpendicular to the cleavage plane. Curves C and C'

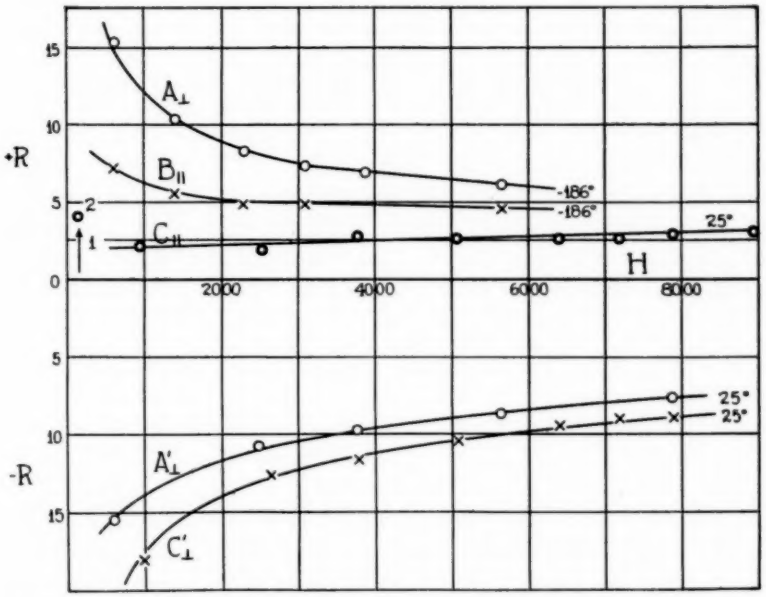

Fig. 1. Variation of the Hall coefficient with magnetic field for different orientations and different temperatures. Note that the inner, extended scale is used for $C_\parallel$.

are for a rectangular bar of dimensions $1.60\times0.34\times0.33$ cm, the length being perpendicular to the trigonal axis and one side of the bar being parallel to the cleavage plane. Curve B is for a plate of dimensions $1.317\times0.513\times0.115$ cm, cut with its plane perpendicular to the trigonal axis of the crystal. At room temperature it was found to give a curve very much like $C_\parallel$.

Consideration of the curves leads to the following conclusions.

1. When the magnetic field is perpendicular to the trigonal axis of the crystal a negative Hall coefficient is observed at room temperatures, a positive coefficient at liquid air temperatures. To secure a general idea of the way in which curve A changed into A' the plate was removed from the

liquid air and the Hall e.m.f. observed as the plate warmed. The field was kept constant at 5700 gauss. In this way it was found that as the plate warmed, R became rapidly smaller, changed sign, and rose to a maximum negative value. This value then decreased slowly to the magnitude given by A' at room temperature.

2. When the field is parallel to the trigonal axis a small positive coefficient is always secured. At room temperature this coefficient increases as the field increases. Other observers have found a negative coefficient in small fields, possibly because of using imperfect crystals, or perhaps because the field was not accurately parallel to the crystal axis. Small departures from parallelism could easily reverse the sign of the Hall effect, since the negative coefficient is about 20 times larger than the positive in small fields.

3. Lowering the temperature of the specimen increases the value of the positive coefficient. The change, however, is not so striking as in the case of the negative coefficient.

4. Curves A' and C' do not coincide. For A' the plate was cut so that the field in the crystal made an angle of 90° with the field used for C'. Another plate cut so as to give the same direction of field as for C' gave the same curve as C'. The difference between C' and A' appears to be too large to ascribe to experimental error; if such is the case the Hall effect does not possess rotational symmetry about the trigonal axis as claimed by van Everdingen. Both Lownds and van Everdingen have observed small differences similar to that between C' and A' but they seem uncertain of the cause. It now appears to be due to differences of structure for the two directions in the crystal.

5. Becquerel's results are not confirmed by the present experiments. From Lownd's experiments we know that the curve $C'_{\perp}$ becomes like $A_{\perp}$ at low temperatures. It thus follows that for all orientations of the crystal at liquid air temperatures the value of R is positive. Becquerel analysed his e.m.f. curves at low temperatures into two components, one positive and following a linear law, the other negative and approaching saturation. No such analysis can be made of the results of the present experiment.

6. At the temperature of liquid air the coefficient of the Hall effect is positive for all field strengths and all orientations of the crystal. A crystal conglomerate should therefore have a positive coefficient at this low temperature.

Beckman[8] experimented with plates of compressed bismuth powder and at the temperature of liquid oxygen found negative values of R ranging from 14.45 to 36.1, depending upon the field and the specimen used. The writer has repeated Beckman's experiment and secured different results.

A piece of the large crystal used in the above experiments was ground to fine powder and compressed in a steel mold. The plate so formed was rectangular and of dimensions $1.95 \times 0.73 \times 0.13$ cm. Electrical connections were made by soldering with Wood's metal. Thin mica cemented with a

[8] B. Beckman, Com. Phys. Lab. Leiden No. 130 (1912).

resin-beeswax mixture was used to protect the specimen from direct contact with the liquid air.

At room temperature this plate gave a negative Hall coefficient, the variation with field being very similar to curve $A'_{\perp}$, but with a value of -5 for $H=7000$. At $-186°$C the coefficient was about $+7$ for all fields greater than 1500. For $H=600$, R was $+8.4$. When the liquid air was removed from the specimen the Hall e m.f. was observed to change sign as the plate warmed, and at room temperature it reached practically the same value it had shown previous to the cooling.

This plate was prepared in the same general way as Beckman's plates; the reason for the disagreement of results is not clear. It is to be noted, however, that a positive coefficient is to be expected from all work on single crystals at low temperatures, and Beckman himself intimates that one of his plates was undoubtedly impure because it had a negative temperature coefficient.

The experiments described in this paper show that it is decidedly incorrect to classify bismuth as a metal with a negative Hall coefficient, though such classification is often made in the literature of the subject.

The writer is indebted to Mr. Maurice Ewing, graduate student in the department of physics, for growing the bismuth crystal used in the experiment, and for doing much preliminary experimental work.

THE RICE INSTITUTE,
HOUSTON, TEXAS.
March 16, 1927.

APPENDIX

At the suggestion of one of the Editors plates A and B were submitted to x-ray and optical examination in order to fix their orientation more exactly than is possible by considering only the position of the normal to the cleavage plane. This work was done by L. W. McKeehan and R. M. Bozorth who report that the plane of plate A is inclined at about 12° to one of the three planes of the form $\{2\bar{1}\bar{1}\}$ (rhombohedral indices), the long dimension being, as intended, nearly parallel to the normal of the (111) plane. The plane of plate B is within 2° of the (111) plane and is at approximately 45° to a $\{2\bar{1}\bar{1}\}$ plane. Crystal A is not quite so perfect as crystal B, possibly because the operation of cutting a thinner plate at a large angle to the cleavage plane produced more distortion in the space-lattice.

THE EFFECT OF WAVE-LENGTH ON THE DIFFERENCES IN THE LAGS OF THE FARADAY EFFECT BEHIND THE MAGNETIC FIELD FOR VARIOUS LIQUIDS

By Fred Allison

Abstract

The lag of the Faraday effect behind the magnetic field was measured by the method of Beams and Allison in carbon bisulphide, toluene, carbon tetrachloride, benzene, xylene, chloroform, and bromoform for various wave-lengths of light from 4481 to 5896A. It is found in every case that the difference in the lags of the Faraday effect behind the magnetic field increases as the wave-length of the light decreases. The extreme magnitudes observed in these time-lag differences range from 0.2×10^{-9} sec. for the longest wave-lengths to 12.2×10^{-9} sec. for the shortest, depending upon the two liquids compared. The precision is about 0.2×10^{-9} sec.

Effect of temperature on the lag of the Faraday effect.—Observations made on carbon bisulphide, toluene and chloroform failed to detect any effect of temperature on the lag of the Faraday effect for temperature differences of 40°C.

Ratio of the speed of electric impulses along wires to the speed of light in air.—The method of the experiment affords a means of measuring the ratio of the speed of electric impulses along copper wires to the speed of light. The value obtained for the ratio was about 96 percent.

IT HAS recently been found by Beams and Allison[1] that the Faraday effect lags behind the magnetic field a longer interval of time in one liquid than in another. The measurement of these time-lag differences could be repeated with a precision of 0.3×10^{-9} sec. The same source of light (the zinc spark lines 4912, 24A) was employed in all the observations.

The investigation has been continued by the writer with the purpose of determining whether this lag in the Faraday effect depends upon the wave-length of light used. It is found[2] in all cases that the time-lag difference for any pair of the liquids increases with decreasing wave-length, or that the differences in the lags of the Faraday effect behind the magnetic field show roughly an inverse variation with the wave-length of light.

The experimental arrangement is the same as that described by Beams and Allison,[1] with some minor improvements whereby the precision of measurement has been somewhat increased. The setup is diagrammatically shown in Fig. 1. The condenser C, the capacity of which could be varied from 5×10^{-4} to 5×10^{-3} microfarads, was charged from an induction coil provided with a Wehnelt interrupter. The spark gap A was so constructed as to allow the ready interchange of the electrodes of the different elements whose spectra served as the sources of light. B_1 and B_2 are cylindrical glass cells which contain the two liquids under observation for time-lag differences. These cells are about 2.5 cm in diameter and 18 cm in length. Each is wound

[1] Beams and Allison, Phys. Rev. **29**, 161 (1927).

[2] Allison, Phys. Rev. **29**, 370 (1927), abstract.

with a helix of 54 turns of No. 18 copper wire. (Subsequently, the cells B_1 and B_2 were made of different dimensions, the length of each being 10 cm, the diameter 2 cm, and each helix consisting of 31 turns of No. 20 copper wire. The determinations made with these cells were in agreement with those made with the original cells.[3] The dimensions of the cells, therefore, do not affect the results, a conclusion which is also supported by other variations of the apparatus mentioned in the sequel.) N_1 and N_2 are Nicol prisms, L is a converging lens and F is a Wratten color filter which transmits light practically monochromatic. T_1T_1 and T_2T_2 are conducting trolleys (strips of brass) which may be shifted back and forth along the lead wires indicated in the diagram, thus changing the lengths of the divided circuits $PT_1B_1T_1P$ and $PT_2B_2T_2P$. This movement of the trolleys is effected by means of a hand wheel mechanism operated by the observer at E.

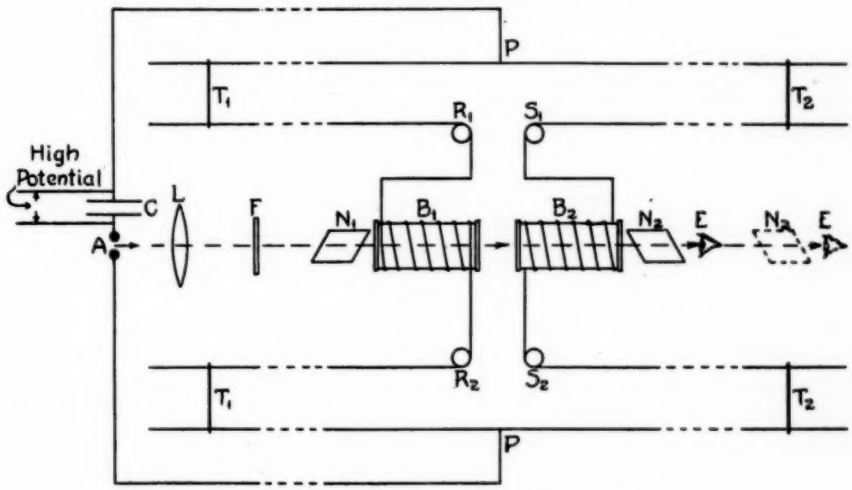

Fig. 1. Diagram of apparatus and connections.

The currents traverse the coils or helices about B_1 and B_2 in opposite directions and establish opposing magnetic fields in the two cells. If, now, the divided circuits $PT_1B_1T_1P$ and $PT_2B_2T_2P$ are such that they are traversed by equal and symmetrical electric impulses when the condenser discharges across A, we shall have the magnetic fields in B_1 and B_2 equal in magnitude and opposite in direction at every instant during their growth and decay. When this condition is realized, the magnetic rotation in one cell is, for any one liquid, completely neutralized by that in the other. This adjustment is attained by first crossing the Nicols N_1 and N_2 and then displacing the trolleys T_1T_1 and T_2T_2 until the light from the spark is completedly extinguished by N_2, when both B_1 and B_2 are filled with the same liquid.

Observations are carried out in the following manner. With B_1 and B_2 temporarily removed, N_2 is rotated until the light from the spark A, made

[3] It should be noted that in very long cells the variation of the refractive index of the liquids with the wave-length of light might in some cases be appreciable, requiring a slight correction in the results.

plane-polorized by N_1, is extinguished. B_1 and B_2 are then filled with, say, carbon bisulphide and replaced in the positions indicated in the diagram. As T_1T_1 or T_2T_2 are moved forward and backward, a point is passed at which the light is completely extinguished to an observer at E. This point of extinction is attributed to the fact that equal and opposite magnetic fields in B_1 and B_2 are applied and relaxed nearly simultaneously (or, more exactly, the field in B_2 is always behind the field in B_1 by a time equal to the distance between the centers of the cells divided by the velocity of light) and therefore that the magnetic rotation in B_1 is annulled by that in B_2.

Carbon bisulphide in B_2 is then replaced by one of the other liquids, toluene, for example, the source of light (the zinc spark lines 4912, 24A), as well as all adjustments, remaining unchanged. Light now passes N_2. But if B_2 is moved backward in the line AN_1N_2 (N_2 is now in the dotted position in order to permit the displacement of B_2 and is always kept crossed with N_1) a distance of 81 cm, a minimum of light passes the Nicol N_2. In other words, as B_2 is moved back and forth, a distinct minimum appears when its displacement from its original position is 81 cm. (The light is not wholly extinguished because the Verdet constant is different for the two liquids.) This observation means that for this particular wave-length the Faraday effect lags behind the magnetic field longer in toluene than in carbon bisulphide by an interval of 2.7×10^{-9} sec. When the spark line Mg 4481A was used, the minimum appeared when B_2 was moved back a distance of 102 cm, giving a time-lag of 3.4×10^{-9} sec. Similarly, the minimum was found for the Cd 5338, 78A spark lines when B_2 was displaced toward E a distance of 33 cm, corresponding to a difference in lag of 1.1×10^{-9} sec. For the D-lines of sodium the displacement of B_2 was only 18 cm, or the time-lag difference was only 0.6×10^{-9} sec. Observations were made in the same manner with other wave-lengths and other pairs of liquids.

In the foregoing method the minima are located by keeping T_1T_1 and T_2T_2 fixed and moving the cell B_2. Determinations of the time-lag difference may also be made with almost the same precision by keeping B_2 fixed in its original position and moving one of the trolleys T_1T_1 or T_2T_2 until the minimum appears. As a representative example of this method, we may refer again to the case of carbon bisulphide and toluene in B_1 and B_2, respectively, with the Mg 4481A spark line as source. The light was found to pass through a minimum when T_2T_2 were displaced toward P a distance of 99 cm. This means that the path of the electric impulse along the straight copper wires is shortened in the branch containing B_2 by 99 cm and consequently that the magnetic field in B_2 is in advance of the field in B_1 by a time required for the electric impulse to travel 99 cm along the bare wires. The same result is obtained if T_1T_1 are moved a distance of 99 cm away from P, T_2T_2 remaining in the original position. It will be noted in the example just cited that the wire-path method gives a value of the time-lag difference 97% of that given by the air-path method. This percentage is itself of interest, in that it represents a direct measurement of the ratio of the speed of the electric impulse in the given wires to the speed of light in air. In as much as the time-

lag differences measured by the air-path and the wire-path methods were found to agree within three or four percent, the latter method has something to recommend it because of the ease and rapidity of locating minima by the displacement of the trolleys instead of the displacement of the cell.

The results of the measurements for the various wave-lengths and liquids are recorded in Table I. Each value is the mean of a number of observations which were taken at different times and with variations in the resistance, capacitance and inductance of the circuit. These changes showed

TABLE I

Lag of the Faraday effect in various liquids behind the lag in carbon bisulphide.

Source	Toluene C_7H_8	Carbon Tetrachlorid CCl_4	Benzene C_6H_6	Xylene C_8H_{10}	Chloroform $CHCl_3$	Bromoform $CHBr_3$
	seconds	seconds	seconds	seconds	seconds	seconds
Mg 4481A	3.4×10^{-9}	4.6×10^{-9}	5.5×10^{-9}	7.3×10^{-9}	8.3×10^{-9}	12.2×10^{-9}
Zn 4722, 4811A	3.2×10^{-9}	4.4×10^{-9}	4.9×10^{-9}	6.4×10^{-9}	7.2×10^{-9}	9.8×10^{-9}
Zn 4912, 24A	2.7×10^{-9}	3.3×10^{-9}	3.5×10^{-9}	4.4×10^{-9}	4.6×10^{-9}	6.6×10^{-9}
Mg 5173, 83A	2.1×10^{-9}	2.6×10^{-9}	2.5×10^{-9}	3.1×10^{-9}	3.3×10^{-9}	4.2×10^{-9}
Cd 5338, 78A	1.1×10^{-9}	1.1×10^{-9}	1.1×10^{-9}	1.3×10^{-9}	1.7×10^{-9}	2.2×10^{-9}
Na 5890, 96A	0.6×10^{-9}	0.6×10^{-9}	0.6×10^{-9}	0.8×10^{-9}	1.2×10^{-9}	1.2×10^{-9}
*Verdet Constant in minutes $\lambda=5890$A	0.0269 (28°C)	0.0321 (15°C)	0.0297 (20°C)	0.0221 (15°C)	0.0164 (20°C)	0.0317 (15°C)

* From the Smithsonian Tables.

no effects on the minima, the time-lag differences obtained under different conditions being in very close agreement. The time interval in each case is the Faraday lag in the specified liquid behind the lag in carbon bisulphide. Observations were also carried out with different pairs of the liquids, as checks on the results, all of which gave consistent values of the time-lag differences.

Each determination recorded in the table was done by both the air-path and the wire-path methods. The results were in consistently closed agreement throughout, showing on the average a lag by air-path about three or four percent greater than by wire-path, or that the speed of the electric impulse in the wire is about 96% or 97% of the speed of light in air. The measurements can be repeated with a precision of about 0.2×10^{-9} sec., depending upon the liquids and upon how nearly the source is monochromatic. The greatest uncertainty attended the location of minima with the Zn 4722, 4811A lines. In many cases, however, the setting on a minimum may be repeated a number of times within 1 cm or 0.3×10^{-10} sec.

It was thought that the presence of the liquids in B_1 and B_2 might possibly exert retardations upon the flow of the electric impulses through the divided circuit, of a different amount for each liquid, which would account, in part at least, for what appeared to be a lag of the Faraday effect. In order to detect the existence of such a retardation four dummy cells, wound with

helices and similar in all essentials to B_1 and B_2, were constructed. Two of these were connected in series in each branched circuit, designated in the diagram by R_1, R_2 and S_1, S_2. If the liquids should exert different retardations upon the electric impulses, the effect would be shown by a change in the setting of B_2(or T_1T_1 or T_2T_2) on the minimum observed before and after the dummy cells are filled with the different liquids, all other adjustments remaining unchanged. Various tests were made with different combinatons of liquids, without any observed effects, the minimum persisting in each case. It was therefore concluded that the liquids do not contribute any influence to the rate of flow of the electric current in the branched circuit.

There are two facts disclosed in these experiments which may account, to some extent, for the failure of other observers to detect a measurable lag in the Faraday effect. One is that the liquid showing the smallest lag is carbon bisulphide, which has usually been the liquid employed in the observations. The other is the fact that the lag is very small for the longer wave-lengths, with which the observations have usually been made.

It will be noted that the time-lag differences herein reported for the zinc spark lines 4912, 24A are larger than those found by Beams and Allison. The discrepancy is to be accounted for by certain refinements in the present method whereby the location of minima are made with greater certainty, along with the use of more nearly monochromatic light.

A temperature effect in the Faraday lag was looked for in carbon bisulphide, toluene and chloroform. A setting on the minimum was made in the usual manner with B_1 and B_2 filled with the liquid, both cells being at the same temperature. The cells were then emptied and refilled with the same liquid, but from vessels kept at different temperatures, one about 40°C above the other. The minimum had not changed, showing therefore no measurable temperature effect.

Oscillations in the circuit were found experimentally not to exist, or at any rate to be too feeble to show any effects.

My acknowledgement is made with pleasure of much indebtedness to Dr. J. W. Beams, National Research Fellow, who suggested this investigation and who has made valuable suggestions during the progress of the work. I wish to thank Professor L. G. Hoxton for his interest in the work and for the loan of equipment.

ALABAMA POLYTECHNIC INSTITUTE,
April 13, 1927.

THE LONGITUDINAL VIBRATIONS OF A LIQUID CONTAINED IN A TUBE WITH ELASTIC WALLS

By T. H. Gronwall

Abstract

This paper investigates the most general longitudinal vibrations of an elastic tube partly filled with liquid. From the rather complicated exact solution of the problem, a simple approximate formula is derived for the reduction of the velocity of sound in the liquid due to the vibrations of the wall of the tube.

1. Introduction

In an experimental investigation of the velocity of sound in liquids now being made by Mr. L. G. Pooler, the following arrangement is used: A vertical steel tube has its upper end free, and its lower end is threaded into a brass holder. The lower end of the tube is closed by a thin steel diaphragm, the edge of which is clamped into the holder, and the lower face of the diaphragm is in contact with an air chamber in which sufficient pressure is maintained to just balance the static pressure of the column of liquid in the tube. The tube stands on the bottom of a tank which may be filled with oil nearly to the top of the tube and the temperature may be held constant by thermostatic control. The diaphragm is now excited electromagnetically to a known frequency, and the tube gradually filled with the liquid to be investigated, and the height of the liquid noted at which resonance occurs. This height is found to vary almost linearly with the reciprocal of the frequency used throughout a wide range. The final readings are taken at the frequency of the free vibrations of the clamped diaphragm.

The velocity of sound c calculated directly from these measurements is appreciably smaller than the velocity c_0 in an unlimited body of the liquid, and it has been already pointed out by Helmholtz[1] that this is due to the elastic vibrations of the tube.

In the present paper, the relation between c and c_0 is obtained from the general equations of elasticity; as is to be expected, it is extremely complicated and takes the form of an infinite determinant set equal to zero. However, the introduction of suitable approximations reduces this equation to a very simple form, the final result being

$$c_0/c=1+y+3y^2+(12-\pi^2/3)y^3+(55-3\pi^2)y^4+\cdots,$$

where the small quantity y is given by

$$y=\frac{\rho_1 c^2}{E}\left(\frac{b^2+a^2}{b^2-a^2}+\sigma\right);$$

here a and b are the interior and exterior radii of the tube, E and σ, Young's modulus and Poisson's ratio for the tube, and ρ_1 the density of the liquid.

[1] Helmholtz, Gesammelte Abhandlungen, v. 1, p. 246.

This problem has been investigated by Lamb and others[2] with the important restrictions that the liquid fills the tube completely, and that the series expansions of the displacements and stresses are limited to a single term; in this manner, Lamb obtains a result which leads to the following expansion

$$c_0/c=1+y+3y^2/2+5y^3/2+35y^4/8+\cdots.$$

This formula leads to smaller values of c_0 than the one given above, the difference being one-tenth of one percent or more, and therefore not negligible.

2. The Longitudinal Vibrations of the Tube

Let a be the interior, b the exterior radius, and l the length of the tube. Using cylindrical coordinates r, θ, z, the z-axis being directed vertically upwards along the axis of the tube, and the origin situated at its lower end, the longitudinal vibrations of the tube are obtained by setting the displacement u_θ equal to zero and assuming the displacements $u_r=u$ and $u_z=w$ to be independent of θ. Writing

$$\Delta=\frac{1}{r}\frac{\partial(ru)}{\partial r}+\frac{\partial w}{\partial z},\qquad 2\varpi=\frac{\partial u}{\partial z}-\frac{\partial w}{\partial r},\tag{1}$$

and denoting the density of the tube by ρ, the equations of vibration are[3]

$$\begin{aligned}\rho\frac{\partial^2 u}{\partial t^2}&=(\lambda+2\mu)\frac{\partial\Delta}{\partial r}+2\mu\frac{\partial\varpi}{\partial z},\\ \rho\frac{\partial^2 w}{\partial t^2}&=(\lambda+2\mu)\frac{\partial\Delta}{\partial z}-\frac{2\mu}{r}\frac{\partial(r\varpi)}{\partial r}.\end{aligned}\tag{2}$$

The stress components are[4]

$$\begin{aligned}&\widehat{rr}=\lambda\Delta+2\mu(\partial u/\partial r), && \widehat{r\theta}=0, && \widehat{rz}=\mu(\partial u/\partial z+\partial w/\partial r),\\ &\widehat{\theta\theta}=\lambda\Delta+2\mu u/r, && \widehat{\theta z}=0, && \widehat{zz}=\lambda\Delta+2\mu(\partial w/\partial z).\end{aligned}\tag{3}$$

Since the lower end of the tube is fixed, and the upper end free, we have the boundary conditions

$$\begin{aligned}&w=0 \text{ at } z=0,\\ &\widehat{zz}=0, \qquad \widehat{rz}=0 \text{ at } z=l.\end{aligned}\tag{4}$$

On the cylindrical boundaries, the shear $\widehat{rz}$ must vanish:

$$\widehat{rz}=0 \text{ at } r=a \text{ and } r=b.\tag{5}$$

[2] H. Lamb, Memoirs and Proceedings of the Manchester Literary and Philosophical Society, vol. 42 (1898), no. 9, where further references are given. See also H. G. Green, Phil. Mag. 45, 907 (1923) who, apparently unaware of Lamb's work, obtains a result which is substantially identical with his.

[3] A. E. H. Love, A Treatise on the Mathematical Theory of Elasticity, 3rd ed. (Cambridge, 1920), p. 291.

[4] Love, l.c., p. 56 and 100.

Moreover,

$$u=u_b \text{ and } \widehat{rr}=-p_b \text{ at } r=b, \tag{6}$$

where u_b is the radial displacement and p_b the pressure of the liquid surrounding the tube, and similarly

$$\begin{aligned} u=u_a \text{ and } \widehat{rr}=-p_a \text{ for } r=a \text{ and } 0\leqq z\leqq h,\\ \widehat{rr}=0 \text{ for } r=a \text{ and } h\leqq z\leqq l, \end{aligned} \tag{7}$$

where h is the height of the liquid in the tube.

Let ν be the frequency of the vibrations, and write $u=Ue^{2\pi i\nu t}$, $w=We^{2\pi i\nu t}$, where U and W are independent of t, and also write

$$\begin{aligned} \Delta&=e^{2\pi i\nu t}(\Delta_1(r)\sin qz+\Delta_2(r)\cos qz),\\ \varpi&=e^{2\pi i\nu t}(\varpi_1(r)\cos qz-\varpi_2(r)\sin qz). \end{aligned} \tag{8}$$

It then follows from (2) that

$$\begin{aligned} -\rho(2\pi\nu)^2U&=[(\lambda+2\mu)(d\Delta_1/dr)-2\mu q\varpi_1]\sin qz+[(\lambda+2\mu)(d\Delta_2/dr)-2\mu q\varpi_2]\cos qz,\\ -\rho(2\mu\nu)^2W&=[(\lambda+2\mu)q\Delta_1-(2\mu/r)(d(r\varpi_1)/dr)]\cos qz-[(\lambda+2\mu)q\Delta_2-(2\mu/r)\\ &\quad\cdot d(r\varpi_2)/dr]\sin qz, \end{aligned} \tag{9}$$

and substituting in (1), it is seen that Δ_1 and Δ_2 must satisfy the differential equation

$$\frac{d^2\Delta}{dr^2}+\frac{1}{r}\frac{d\Delta}{dr}-\left(q^2-\frac{\rho(2\pi\nu)^2}{\lambda+2\mu}\right)\Delta=0 \tag{10}$$

while ϖ_1 and ϖ_2 satisfy the equation

$$\frac{d^2\varpi}{dr^2}+\frac{1}{r}\frac{\partial\varpi}{dr}-\left(\frac{1}{r^2}+q^2-\frac{\rho(2\pi\nu)^2}{\mu}\right)\tilde{\omega}=0. \tag{11}$$

From the first of (4) and the second of (9), it now follows that

$$\Delta_1=\frac{2\mu}{(\lambda+2\mu)qr}\frac{d(r\tilde{\omega}_1)}{dr};$$

substituting in (10) and reducing by means of (11), it is readily seen that $\varpi_1=0$, so that $\Delta_1=0$. Calculating zz from (3), it follows that in order to make $\widehat{zz}$ vanish at $z=l$, we must have $\cos ql=0$ or

$$q=q_n=\frac{2n+1}{2}\frac{\pi}{l}. \tag{12}$$

Writing

$$\begin{aligned} \alpha_n^2&=q_n^2-\frac{\rho(2\pi\nu)^2}{\lambda+2\mu},\\ \beta_n^2&=q_n^2-\frac{\rho(2\pi\nu)^2}{\mu}, \end{aligned} \tag{13}$$

equations (8) to (11) show that the most general solution of (1) and (2) satisfying the first two boundary conditions (4) are

$$
\begin{aligned}
e^{-2\pi i\nu t}\Delta &= \sum_{n=0}^{n=\infty} \left[A_n I_0(\alpha_n r)+B_n K_0(\alpha_n r)\right] \cos q_n z,\\
e^{-2\pi i\nu t}\varpi &= -\sum_{n=0}^{n=\infty} \left[C_n I_1(\beta_n r)+D_n K_1(\beta_n r)\right] \sin q_n z,\\
e^{-2\pi i\nu t}\cdot\rho(2\pi\nu)^2 u &= \sum_{n=0}^{n=\infty} \{-(\lambda+2\mu)\alpha_n\left[A_n I_1(\alpha_n r)-B_n K_1(\alpha_n r)\right]\\
&\qquad +2\mu q_n\left[C_n I_1(\beta_n r)+D_n K_1(\beta_n r)\right]\} \cos q_n z,\\
e^{-2\pi i\nu t}\cdot\rho(2\pi\nu)^2 w &= \sum_{n=0}^{n=\infty} \{(\lambda+2\mu) q_n\left[A_n I_0(\alpha_n r)+B_n K_0(\alpha_n r)\right]\\
&\qquad -2\mu\beta_n\left[C_n I_0(\beta_n r)-D_n K_0(\beta_n r)\right]\} \sin q_n z.
\end{aligned}
\tag{14}
$$

From (3) and (14) we obtain

$$
\begin{aligned}
e^{-2\pi i\nu t}\cdot\frac{\rho(2\pi\nu)^2}{2\mu}\widehat{rz} = \sum_{n=0}^{n=\infty} &\{(\lambda+2\mu)\alpha_n q_n\left[A_n I_1(\alpha_n r)-B_n K_1(\alpha_n r)\right]\\
&-\mu(\beta_n^2+q_n^2)\left[C_n I_1(\beta_n r)+D_n K_1(\beta_n r)\right]\} \cos q_n z,
\end{aligned}
$$

and boundary conditions (5) become

$$
\begin{aligned}
&\frac{(\lambda+2\mu)\alpha_n q_n}{\mu(\beta_n^2+q_n^2)}\left[A_n I_1(\alpha_n a)-B_n K_1(\alpha_n a)\right]-C_n I_1(\beta_n a)-D_n K_1(\beta_n a)=0,\\
&\frac{(\lambda+2\mu)\alpha_n q_n}{\mu(\beta_n^2+q_n^2)}\left[A_n I_1(\alpha_n b)-B_n K_1(\alpha_n b)\right]-C_n I_1(\beta_n b)-D_n K_1(\beta_n b)=0.
\end{aligned}
\tag{15}
$$

From the expression above for $\widehat{rz}$ it is seen that the last boundary condition (4) is not satisfied except at $r=a$, $r=b$; this circumstance is a familiar one in all problems where one or both ends of a cylinder are free, and cannot be avoided.

Using equations (15) to simplify the expression for u in (14) at $r=a$ and $r=b$, we find

$$
e^{-2\pi i\nu t}u = \sum_{n=0}^{n=\infty} \frac{\lambda+2\mu}{\mu}\,\frac{\alpha_n}{\beta_n^2+q_n^2}\left[A_n I_1(\alpha_n r)-B_n K_1(\alpha_n r)\right] \cos q_n z, \qquad r=a \text{ or } r=b,
\tag{16}
$$

and treating the expression for $\widehat{rr}$ obtained from (3) and (14) in the same manner,

$$
\begin{aligned}
e^{-2\pi i\nu t}\cdot\rho(2\pi\nu)^2\widehat{rr} = \sum_{n=0}^{n=\infty} &\{-\mu(\lambda+2\mu)(\beta_n^2+q_n^2)\left[A_n I_0(\alpha_n r)+B_n K_0(\alpha_n r)\right]\\
&-2\rho(2\pi\nu)^2\frac{(\lambda+2\mu)\alpha_n}{\beta_n^2+q_n^2}\left[A_n\frac{I_1(\alpha_n r)}{r}-B_n\frac{K_1(\alpha_n r)}{r}\right]\\
&+4\mu^2\beta_n q_n\left[C_n I_0(\beta_n r)-D_n K_0(\beta_n r)\right]\} \cos q_n z,
\end{aligned}
\tag{17}
$$

$r=a$ or $r=b$.

3. *The longitudinal vibrations of the liquid outside the tube.* Let p be the excess of the pressure of the liquid over the hydrostatic pressure, then the density ρ' of the liquid is given by

$$\rho' = \rho_0[1+(p/\kappa_0)], \tag{18}$$

where ρ_0 is the hydrostatic density and κ_0 the cubical elasticity of the liquid. The hydrodynamical equations are[5]

$$\begin{aligned} -\partial p/\partial r &= \rho'(\partial^2 u/\partial t^2), \\ -\partial p/\partial z &= \rho'(\partial^2 w/\partial t^2), \end{aligned} \tag{19}$$

and the equation of continuity

$$\frac{\partial \rho'}{\partial t} + \frac{1}{r}\frac{\partial}{\partial r}\left(r\rho'\frac{\partial u}{\partial t}\right) + \frac{\partial}{\partial z}\left(\rho'\frac{\partial w}{\partial t}\right) = 0 \tag{20}$$

Since p/κ_0 is small, we may replace ρ' by ρ_0 in (19) and in the last two terms in (20); writing $p = P(r)e^{2\pi i\nu t+qiz}$, $u = U(r)e^{2\pi i\nu t+qiz}$, $w = W(r)e^{2\pi i\nu t+qiz}$, it is seen from (19) that

$$\rho_0(2\pi\nu)^2 U = dP/dr, \qquad \rho_0(2\pi\nu)^2 W = qiP \tag{21}$$

and (20) becomes

$$\frac{d^2P}{dr^2} + \frac{1}{r}\frac{dP}{dr} - \left(q^2 - \frac{\rho_0(2\pi\nu)^2}{\kappa_0}\right)P = 0. \tag{22}$$

The boundary conditions are (6) and

$$\begin{aligned} &w = 0 \text{ at } z = 0, \qquad p = 0 \text{ at } z = l, \\ &p \text{ finite as } r \to \infty\ ; \end{aligned} \tag{23}$$

conditions (23) are satisfied by giving q the values q_n defined by (12), and making

$$e^{-2\pi i\nu t}p = \sum_{n=0}^{n=\infty} F_n K_0(\gamma_n r)\cos q_n z \tag{24}$$

where

$$\gamma_n^2 = q_n^2 - \rho_0(2\pi\nu)^2/\kappa_0. \tag{25}$$

From (24) it follows that

$$e^{-2\pi i\nu t}\cdot\rho_0(2\pi\nu)^2 u = -\sum_{n=0}^{n=\infty}\gamma_n F_n K_1(\gamma_n r)\cos q_n z \tag{26}$$

and using (16) and (17), the boundary conditions (6) become

$$-\gamma_n F_n K_1(\gamma_n b) = \rho_0(2\pi\nu)^2\frac{\lambda+2\mu}{\mu}\frac{\alpha_n}{\beta_n^2+q_n^2}[A_n I_1(\alpha_n b) - B_n K_1(\alpha_n b)],$$

$$\rho(2\pi\nu)^2 F_n K_0(\gamma_n b) = -\mu(\lambda+2\mu)(\beta_n^2+q_n^2)[A_n I_0(\alpha_n b) + B_n K_0(\alpha_n b)]$$

[5] See Lamb's Hydrodynamics, 4th ed., chapter I.

$$-2\rho(2\pi\nu)^2\frac{(\lambda+2\mu)\alpha_n}{\beta_n^2+q_n^2}\left[A_n\frac{I_1(\alpha_n b)}{b}-B_n\frac{K_1(\alpha_n b)}{b}\right]$$
$$+4\mu^2\beta_n q_n\left[C_n I_0(\beta_n b)-D_n K_0(\beta_n b)\right].$$

Eliminating F_n between the last two equations we obtain

$$\left[-c_n I_0(\alpha_n b)+\left(\frac{\rho_0(2\pi\nu)^2 d_n}{2\mu}\frac{K_0(\gamma_n b)}{\gamma_n K_1(\gamma_n b)}-\frac{d_n}{b}\right)I_1(\alpha_n b)\right]A_n$$
$$+\left[-c_n K_0(\alpha_n b)+\left(\frac{d_n}{b}-\frac{\rho_0(2\pi\nu)^2 d_n}{2\mu}\frac{K_0(\gamma_n b)}{\gamma_n K_1(\gamma_n b)}\right)K_1(\alpha_n b)\right]B_n$$
$$+f_n I_0(\beta_n b)C_n-f_n K_0(\beta_n b)D_n=0 \tag{27}$$

with the following notations

$$c_n=\mu(\lambda+2\mu)(q_n^2+\beta_n^2), \qquad f_n=4\mu^2 q_n\beta_n,$$
$$d_n=2\rho(2\pi\nu)^2\frac{(\lambda+2\mu)\alpha_n}{q_n^2+\beta_n^2}, \qquad \Gamma_n=\frac{(\lambda+2\mu)q_n\alpha_n}{\mu(q_n^2+\beta_n^2)}. \tag{28}$$

On account of the smallness of the ratio $(2\pi\nu)^2/\mu$, the terms in (27) containing γ_n may be neglected.[6]

From (27), (28) and (15), it is seen that A_n, B_n, $-C_n$ and $-D_n$ are proportional to the minors of the first row of either of the following determinants

$$\phi_n=\begin{vmatrix} -c_n I_0(\alpha_n a)-\frac{d_n}{a}I_1(\alpha_n a), & -c_n K_0(\alpha_n a)+\frac{d_n}{a}K_1(\alpha_n a), & -f_n I_0(\beta_n a), & f_n K_0(\beta_n a) \\ -c_n I_0(\alpha_n b)-\frac{d_n}{b}I_1(\alpha_n b), & -c_n K_0(\alpha_n b)+\frac{d_n}{b}K_1(\alpha_n b), & -f_n I_0(\beta_n b), & f_n K_0(\beta_n b) \\ \Gamma_n I_1(\alpha_n a), & -\Gamma_n K_1(\alpha_n a), & I_1(\beta_n a), & K_1(\beta_n a) \\ \Gamma_n I_1(\alpha_n b), & -\Gamma_n K_1(\alpha_n b), & I_1(\beta_n b), & K_1(\beta_n b) \end{vmatrix}$$

$$\frac{\mu(q_n^2+\beta_n^2)}{(\lambda+2\mu)\alpha_n}\cdot\psi_n=$$

$$\begin{vmatrix} I_1(\alpha_n a), & -K_1(\alpha_n a), & 0, & 0 \\ -c_n I_0(\alpha_n b)-\frac{d_n}{b}I_1(\alpha_n b), & -c_n K_0(\alpha_n b)+\frac{d_n}{b}K_1(\alpha_n b), & -f_n I_0(\beta_n b), & f_n K_0(\beta_n b) \\ \Gamma_n I_1(\alpha_n a), & -\Gamma_n K_1(\alpha_n a), & I_1(\beta_n a), & K_1(\beta_n a) \\ \Gamma_n I_1(\alpha_n b), & -\Gamma_n K_1(\alpha_n b), & I_1(\beta_n b), & K_1(\beta_n b) \end{vmatrix} \tag{29}$$

Writing G_n for the proportionality factor, it follows from (16), (17) and (29) that for $r=a$

[6] Making $n=0$, the largest value of $K_0(\gamma_n b)/b\gamma_n K_1(\gamma_n b)$ occurring in the experimental work is about 12, and the largest value of $\rho_0(2\pi\nu)^2/2\mu$ is 1.5×10^{-4}.

$$e^{-2\pi i\nu t}\cdot\rho(2\pi\nu)^2\,\widehat{rr}=\sum_{n=0}^{n=\infty}G_n\phi_n\cos q_nz,$$
$$e^{-2\pi i\nu t}u=\sum_{n=0}^{n=\infty}G_n\psi_n\cos q_nz. \tag{30}$$

4. *The longitudinal vibrations of the liquid inside the tube.* Replacing ρ_0 and κ_0 by the corresponding values ρ_1 and κ_1 for the liquid inside the tube, denoting by h the height of the liquid at which resonance occurs, and observing that when this is the case, no force is transmitted from the diaphragm to the liquid, it is seen that the boundary conditions at the ends of the liquid column are

$$p=0 \text{ at } z=0 \text{ and } z=h. \tag{31}$$

Moreover, p must be finite at $r=0$. It is then seen, exactly as at the beginning of paragraph 3, that p is given by

$$e^{-2\pi i\nu t}p=\sum_{s=1}^{s=\infty}H_sI_0(\delta_sr)\sin(\pi msz/h), \tag{32}$$

where

$$\delta_s^2=\left(\frac{\pi ms}{h}\right)^2-\frac{\rho_1(2\pi\nu)^2}{\kappa_1}, \tag{33}$$

and $m=1$ for the fundamental vibration (corresponding to the smallest value of h for which resonance occurs), while $m=2, 3, \cdots$, for the successive higher harmonics. From (32) and the first of (19), it now follows that

$$e^{-2\pi i\nu t}\cdot\rho_1(2\pi\nu)^2u=\sum_{s=1}^{s=\infty}H_s\delta_sI_1(\delta_sr)\sin(\pi msz/h). \tag{34}$$

There now remain to be satisfied only the boundary conditions (7). Since the functions $(2/l)^{1/2}\cos q_nz$ are orthogonal and normalized with respect to the interval $0\leqq z\leqq l$, it follows from the first of (30) that for $r=a$

$$G_n\phi_n=2/l\cdot\rho(2\pi\nu)^2\int_0^l e^{-2\pi i\nu t}\,\widehat{rr}\cos q_nz\,dz,$$

and since $\widehat{rr}=-p_a$ for $0\leqq z\leqq h$, but $\widehat{rr}=0$ for $h\leqq z\leqq l$ by (7), we obtain by making $r=a$ in (32)

$$G_n\phi_n=-2/l\cdot\rho(2\pi\nu)^2\int_0^h\sum_{s=1}^{s=\infty}H_sI_0(\delta_sa)\sin(\pi msz/h)\cos q_nz\,dz.$$

Writing

$$a_{ns}=\int_0^h\sin(\pi msz/h)\cos q_nz\,dz, \tag{35}$$

the preceding equation becomes

$$G_n\phi_n = -2/l \cdot \rho(2\pi\nu)^2 \sum_{s=1}^{s=\infty} H_s I_0(\delta_s a) a_{ns}. \tag{36}$$

Since the functions $\sin \pi msz/h$ are orthogonal in the interval $0 \leqq z \leqq h$, it is seen from (34) that

$$H_s\delta_s I_1(\delta_s a) = 2/h \cdot \rho_1(2\pi\nu)^2 \int_0^h e^{-2\pi i\nu t} u_a \sin(\pi msz/h)\, dz,$$

and according to (7), u_a is to be replaced by the second expression (30); with the aid of (35) this gives, upon replacing the summation subscript n by n_1,

$$H_s\delta_s I_1(\delta_s a) = 2/h \cdot \rho_1(2\pi\nu)^2 \sum_{n_1=0}^{n_1=\infty} G_{n_1}\psi_{n_1} a_{n_1 s}. \tag{37}$$

Solving (37) for H_s, substituting in (36) and writing $G_n\phi_n = x_n$ we obtain the following infinite system of linear equations in $x_0, x_1, x_2, \cdots$

$$x_n + \sum_{n_1=0}^{n_1=\infty} c_{nn_1} x_{n_1} = 0 \qquad (n = 0,1,2,\cdots) \tag{38}$$

where

$$c_{nn_1} = (4/hl) \cdot \rho\rho_1(2\pi\nu)^4 (\psi_{n_1}/\phi_{n_1}) \sum_{s=1}^{s=\infty} a_{ns} \cdot a_{n_1 s} I_0(\delta_s a)/\delta_s I_1(\delta_s a). \tag{39}$$

Since all G_n do not vanish, (38) must have a solution where all x_n do not vanish, and consequently the infinite determinant of the system must vanish, or

$$\begin{vmatrix} 1+c_{00}, & c_{01}, & c_{02}, & \cdots \\ c_{10}, & 1+c_{11}, & c_{12}, & \cdots \\ c_{20}, & c_{21}, & 1+c_{22}, & \cdots \\ \cdots, & \cdots, & \cdots, & \cdots \end{vmatrix} = 0, \tag{40}$$

and this is the desired equation connecting ν and h in the case of resonance. We shall now introduce successively such approximations as will reduce (40) to a numerically manageable form.

5. *Approximate expressions for the quotient* ψ_n/ϕ_n. First assume $\alpha_n a, \beta_n a, \alpha_n b, \beta_n b$ to be small, and replace the Bessel functions by the principal parts of their power series expansions;[7] it then follows from (29) that the principal part of ϕ_n is

$$\begin{vmatrix} -c_n - \tfrac{1}{2}d_n\alpha_n, & -d_n/a^2\alpha_n, & -f_n, & f_n \log \alpha_n a \\ -c_n - \tfrac{1}{2}d_n\alpha_n, & -d_n/b^2\alpha_n, & -f_n, & f_n \log \alpha_n b \\ \tfrac{1}{2}\Gamma_n\alpha_n a, & -\Gamma_n/a\alpha_n, & \tfrac{1}{2}\beta_n a, & 1/a\beta_n \\ \tfrac{1}{2}\Gamma_n\alpha_n b, & -\Gamma_n/b\alpha_n, & \tfrac{1}{2}\beta_n b, & 1/b\beta_n \end{vmatrix}$$

[7] G. N. Watson, A Treatise on the Theory of Bessel's Functions, Cambridge 1922, pp. 77–80.

$$=ab\left(\frac{1}{a^2}-\frac{1}{b^2}\right)\left(\frac{\Gamma_n f_n\alpha_n}{\beta_n}-c_n-\frac{d_n\alpha_n}{2}\right)\left[\frac{d_n}{2\alpha_n}\left(\frac{1}{a^2}-\frac{1}{b^2}\right)+\frac{\Gamma_n f_n\beta_n}{2\alpha_n}\log\frac{b}{a}\right].$$

Referring to (28) and observing that for n small, the quotient $2\mu q_n^4/\rho(2\pi\nu)^2$ is small for the values of l and ν used in the experiments, it is seen that the second term in the square bracket above is negligible in comparison to the first. We may therefore write, approximately,

$$\phi_n=ab\left(\frac{1}{a^2}-\frac{1}{b^2}\right)^2\frac{d_n}{2\alpha_n}\left(\frac{\Gamma_n f_n\alpha_n}{\beta_n}-c_n-\frac{d_n\alpha_n}{2}\right),$$

and treating ψ_n in the same manner,

$$-\psi_n=b\left(\frac{1}{a^2}-\frac{1}{b^2}\right)\frac{\lambda+2\mu}{2\mu(q_n^2+\beta_n^2)}\left[\frac{\Gamma_n f_n\alpha_n}{\beta_n}-c_n+\left(\frac{a^2}{b^2}-1\right)\frac{d_n\alpha_n}{2}\right].$$

Using (28), and introducing Young's modulus E and Poisson's ratio σ by the equations

$$E=\mu(3\lambda+2\mu)/(\lambda+\mu), \qquad \sigma=\lambda/2(\lambda+\mu),$$

the preceding expressions for ϕ_n and ψ_n give

$$-\rho(2\pi\nu)^2\frac{\psi_n}{\phi_n}=\frac{1}{E}\cdot\frac{a}{\frac{b}{a}-\frac{a}{b}}\left[\frac{b}{a}+\frac{a}{b}+\sigma\left(\frac{b}{a}-\frac{a}{b}\right)+2\sigma^2\frac{a}{b}\left\{\frac{E}{\rho}\left(\frac{q_n}{2\pi\nu}\right)^2-1\right\}^{-1}\right],$$

or neglecting the last term in the bracket, which is small compared to the others,

$$-\rho(2\pi\nu)^2\frac{\psi_n}{\phi_n}=\frac{a}{E}\left(\frac{b^2+a^2}{b^2-a^2}+\sigma\right). \tag{41}$$

For larger values of n, we calculate α_n and β_n from (13) by the binomial theorem and retain the first two terms only :

$$\alpha_n=q_n-[\rho(2\pi\nu)^2]/[2q_n(\lambda+2\mu)],$$
$$\beta_n=q_n-[\rho(2\pi\nu)^2]/2q_n\mu.$$

We then expand $I_0(\alpha_n a)$by Taylor's theorem to two terms, so that since $I_0'(x)=I_1(x)$,

$$I_0(\alpha_n a)=I_0(q_n a)-\frac{\rho(2\pi\nu)^2 a}{2q_n(\lambda+2\mu)}\cdot I_1(q_n a),$$

and proceed similarly for the other Bessel functions. Expanding also the constants in (28) in the same manner, introducing all expansions in (29) and discarding terms containing higher powers of $1/q_n$ than the first, a somewhat lengthy but not otherwise difficult calculation gives

$$-\rho(2\pi\nu)^2\frac{\psi_n}{\phi_n}=\frac{2(1-\sigma^2)a}{E}\cdot\frac{\bar{\psi}_n}{\bar{\phi}_n}, \tag{42}$$

where

$$\begin{aligned}\bar{\phi}_n&=[Q(q_na)-Q(q_nb)][R(q_na)-R(q_nb)]-[P(q_na)-P(q_nb)]^2,\\ \bar{\psi}_n&=Q(q_nb)I_1(q_na)^2+2P(q_nb)I_1(q_na)K_1(q_na)+R(q_nb)K_1(q_na)^2-1,\end{aligned} \tag{43}$$

and the functions P, Q, and R are defined by

$$\begin{aligned}P(x)&=x^2[I_0(x)K_0(x)+I_1(x)K_1(x)]+2(1-\sigma)I_1(x)K_1(x),\\ Q(x)&=x^2[K_0(x)^2-K_1(x)^2]-2(1-\sigma)K_1(x)^2,\\ R(x)&=x^2[I_0(x)^2-I_1(x)^2]-2(1-\sigma)I_1(x)^2,\end{aligned} \tag{44}$$

so that

$$P(x)^2-Q(x)R(x)=x^2+2(1-\sigma). \tag{45}$$

Substituting the leading terms in the power series expansions of the Bessel functions in (43) and (44), it is readily seen that (42) reduces to (41). But it is also found by numerical calculation that the expression (42) varies slowly as n increases; for $n=0$, (42) differs from (41) in the seventh significant figure only, while for $n=5$ and $n=10$, the difference is about a unit in the fourth and third significant figures, respectively. Finally, for n very large, we substitute the asymptotic expansions of the Bessel functions[8] either in (44), (43) and (42) or directly in the determinants (29), and obtain

$$-\rho(2\pi\nu)^2\psi_n/\phi_n=2(1-\sigma^2)/Eq_n. \tag{46}$$

When the tube is thin (the ratio $(b-a)/a$ being less than 0.15) and n is small, the expression (41) for ψ_n/ϕ_n is inaccurate. A good approximation is however obtained by expanding the second and fourth rows in the determinant (29) in powers of $b-a$, and limiting the expansion to two terms. After some simple transformations, either determinant reduces to the product of two second order determinants, from which the Bessel functions disappear in consequence of the relation $I_0(x)K_1(x)+I_1(x)K_0(x)=1/x$, and we obtain

$$\begin{aligned}\phi_n=\frac{(b-a)^2}{a^2}\,&\frac{\lambda+2\mu}{(q_n^2+\beta_n^2)^2}\rho^2(2\pi\nu)^4\left\{\frac{4}{a^2}\left[(3\lambda+2\mu)q_n^2-\frac{\lambda+\mu}{\mu}\rho(2\pi\nu)^2\right]\right.\\ &\left.-4q_n^2\rho(2\pi\nu)^2\frac{\lambda+\mu}{\mu}+\frac{\lambda+2\mu}{\mu^2}\rho^2(2\pi\nu)^4\right\},\\ -\psi_n=\frac{b-a}{a^2}\,&\frac{\lambda+2\mu}{(q_n^2+\beta_n^2)^2}\rho(2\pi\nu)^2\left[4q_n^2\frac{\lambda+\mu}{\mu}-\frac{\lambda+2\mu}{\mu^2}\rho(2\pi\nu)^2\right],\end{aligned}$$

or retaining only the first term in each bracket,

$$-\rho(2\pi\nu)^2\frac{\psi_n}{\phi_n}=\frac{1}{E}\left(\frac{1}{2\sigma}-1\right)\frac{a^2}{b-a}. \tag{41a}$$

[8] Watson, l.c., pp. 202–203.

6. *Reduction of the infinite determinant* (40). Expanding the determinant by Laplace's formula, we find

$$1+\sum_{n=0}^{n=\infty} c_{nn}+\sum_{\substack{n,n_1=0\\ n<n_1}}^{n,n_1=\infty}\begin{vmatrix} c_{nn}, & c_{nn_1}\\ c_{n_1n}, & c_{n_1n_1}\end{vmatrix}$$

$$+\sum_{\substack{n,n_1,n_2=0\\ n<n_1<n_2}}^{n,n_1,n_2=\infty}\begin{vmatrix} c_{nn}, & c_{nn_1}, & c_{nn_2}\\ c_{n_1n}, & c_{n_1n_1}, & c_{n_1n_2}\\ c_{n_2n}, & c_{n_2n_1}, & c_{n_2n_2}\end{vmatrix}+\cdots=0.$$

From (39), (41), (42) and (46) it is seen that every c_{nn_1} contains the small factor $(2\pi\nu)^2/E$. Consequently, the second and following sums above contain the square, cube, $\cdots$ of this factor, and may be neglected in comparison to the first, so that (40) reduces to

$$1+\sum_{n=0}^{n=\infty} c_{nn}=0,$$

or, by (39)

$$1+\sum_{s=1}^{s=\infty}\frac{4\rho_1(2\pi\nu)^2}{hl}\,\frac{I_0(\delta_s a)}{\delta_s I_1(\delta_s a)}\sum_{n=0}^{n=\infty}\rho(2\pi\nu)^2\frac{\psi_n}{\phi_n}a_{ns}{}^2=0. \tag{47}$$

If we replace $-\rho(2\pi\nu)^2\psi_n/\phi_n$ by the expression (41) which is independent of n, it is seen from (46) that this value is too large when n is large, so that the sum with respect to n in (47) becomes too large numerically. We may compensate this error, at least in part, by replacing $I_0(\delta_s a)/\delta_s I_1(\delta_s a)$ by $2/\delta_s{}^2 a$ which is too small when δ_s is large, the asymptotic value of $I_0(\delta_s a)/\delta_s I_1(\delta_s a)$ being $1/\delta_s$. With these substitutions, (47) becomes

$$1-\frac{8\rho_1(2\pi\nu)^2}{hl}\cdot\frac{1}{E}\left(\frac{b^2+a^2}{b^2-a^2}+\sigma\right)\sum_{s=1}^{s=\infty}\frac{1}{\delta_s{}^2}\sum_{n=0}^{n=\infty}a_{ns}{}^2=0.$$

By (35), $(2/l)^{1/2}a_{ns}$ $(n=0, 1, 2, \cdots)$ are the Fourier coefficients with respect to the orthogonal and normalized functions $(2/l)^{1/2}\cos q_n z$ of a function $f(z)$ which equals $\sin(\pi msz/h)$ for $0\leqq z\leqq h$, but vanishes for $h\leqq z\leqq l$; hence Parseval's theorem gives

$$(2/l)\sum_{n=0}^{n=\infty}a_{ns}{}^2=\int_0^l f(z)^2\,dz$$

$$=\int_0^h\sin^2(\pi msz/h)\,dz=h/2,$$

and the preceding equation becomes

$$1-\frac{2\rho_1(2\pi\nu)^2}{E}\left(\frac{b^2+a^2}{b^2-a^2}+\sigma\right)\sum_{s=1}^{s=\infty}\frac{1}{\delta_s{}^2}=0. \tag{48}$$

To calculate the sum occurring in (48), we observe that the velocity of sound c_0 in an unlimited body of the liquid contained in the tube is given by

$$c_0^2=\kappa_1/\rho_1, \tag{49}$$

while the uncorrected velocity c is given by the experiment as

$$c=2\nu h/m. \tag{50}$$

From (33), (49) and (50) we find

$$\sum_{s=1}^{s=\infty}\frac{1}{\delta_s^2}=\left(\frac{c}{2\pi\nu}\right)^2\sum_{s=1}^{s=\infty}\frac{1}{s^2-(c/c_0)^2},$$

and from the well known formula

$$\pi\cot\pi x=1/x+\sum_{s=1}^{s=\infty}2x/(x^2-s^2)$$

it follows that

$$\sum_{s=1}^{s=\infty}\frac{1}{\delta_s^2}=\left(\frac{c}{2\pi\nu}\right)^2\cdot\frac{c_0}{2c}\left[\frac{c_0}{c}-\pi\cot\pi\frac{c}{c_0}\right]. \tag{51}$$

We introduce the notation

$$y=\frac{\delta_1 c^2}{E}\left(\frac{b^2+a^2}{b^2-a^2}+\sigma\right), \tag{52}$$

and write

$$c_0=c/(1-\epsilon)\ ; \tag{53}$$

by means of (51), (52) and (53) it is now seen that (48) becomes

$$\frac{(1-\epsilon)^2}{1+(1-\epsilon)\pi\cot\pi\epsilon}=y$$

Introducing the expansion $\cot\pi\epsilon=1/\pi\epsilon-\pi\epsilon/3-\cdots$, and expanding the left hand member in the equation above in powers of ϵ, we find

$$\epsilon-2\epsilon^2+(1+\pi^2/3)\epsilon^3-\pi^2\epsilon^4+\cdots=y. \tag{54}$$

Inverting the power series, it is seen that

$$\epsilon=y+2y^2+(7-\pi^2/3)y^3+(30-7\pi^2/3)y^4+\cdots, \tag{55}$$

and for the correction factor $1/(1-\epsilon)$, by which the measured velocity of sound c has to be multiplied according to (53) in order to give the velocity of sound c_0 in an unlimited body of the liquid, (55) now gives

$$\begin{aligned}1/(1-\epsilon)=1+y+3y^2+(12-\pi^2/3)y^3+(55-3\pi^2)y^4\\+(1428-455\pi^2/3+137\pi^4/15)y^5+\cdots.\end{aligned} \tag{56}$$

In the case of a thin tube, $(b-a)/a<0.15$, the approximation (41) to $\rho(2\pi\nu)^2\psi_n/\phi_n$ is not valid for small values of n, for which it should be replaced by (41a).

For the two thin tubes used in the experimental work, $(b-a)/a=0.148$ and 0.067 respectively, and numerical calculation shows that in both cases, a good approximation to the sum with respect to n in (47) is obtained by using (41a) for $n \leqq n_1$, where n_1 is the greatest value of n for which

$$\sum_{n=0}^{n=n_1} a_{ns}^2 \leqq \frac{1}{3} \sum_{n=0}^{n=\infty} a_{ns}^2 ;$$

for $n>n_1$, (41) is used as before. It is seen at once that this amounts to replacing (52) by

$$y=\frac{\rho_1 c^2}{E}\left[\frac{2}{3}\left(\frac{b^2+a^2}{b^2-a^2}+\sigma\right)+\frac{1}{3}\left(\frac{1}{2\sigma}-1\right)\frac{a}{b-a}\right]; \tag{52a}$$

equations (55) and (56) of course remain unchanged.

In the paper quoted in the introduction, Lamb limits all expansions such as (14) to a single term, and his final formula (66) is equivalent to retaining only the first term, $s=1$, in our equation (48). The relation between y and ϵ then becomes

$$\epsilon-\tfrac{1}{2}\epsilon^2=y,$$

whence

$$1/(1-\epsilon)=1/(1-2y)^{1/2}=1+y+3y^2/2+5y^3/2+35y^4/8+\cdots .$$

DEPARTMENT OF PHYSICS,
COLUMBIA UNIVERSITY,
February 28, 1927.

FACTORIAL FUNCTIONS IN ENTROPY CALCULATIONS

By Morton Masius

Abstract

In entropy calculations in connection with the kinetic theory of gases or the quantum theory the changes in functions depending on factorials have hitherto been calculated by a method depending on the replacement of factorials by continuous functions and differentiation. This method is neither simple nor logically satisfying. A new method of calculation is shown which depends on the direct evaluation, by simple well known processes, of

$$\Delta F = F(x+\Delta x, y+\Delta y, \cdots) - F(x,y, \cdots)$$

where F is a function involving the factorials of $x, y, \cdots$, and where $x, y, \cdots$ and $x+\Delta x, y+\Delta y, \cdots$ are taken as integers. The details of this method are illustrated by the treatment of two examples.

IN the relation $S=k \lg W$, which occurs in the kinetic theory and, with a slightly different significance, in the quantum theory, and in which S denotes the entropy of the state and k a universal constant, the quantity W, the probability of the state, is always an expression involving factorials. It sometimes becomes necessary to consider a change in S brought about by a change in W. This has usually been done by replacing, with the aid of Stirling's theorem, the discontinuous factorials, which are defined only for integral values of their arguments and which are contained in W, by continuous functions, and then calculating the changes in S by differentiation. This method of procedure involves some not quite obvious mathematics. Moreover the results obtained are cumbersome and have to be simplified by considering the relative size of the terms and neglecting in successive approximations all terms that are relatively small. Usually four or five approximations are necessary in the process, and the cumulative result of these can not easily be traced. Lastly, this method requires us to think of quantities, gas molecules or energy quanta, which by their nature are discrete finite quantities, capable of changes in finite steps only, as continuously variable. The method outlined in the following requires only simple mathematical processes, it leads to the final result with fewer approximations, as a rule only one approximation is required, and it allows us to treat the number of gas molecules or energy quanta as integers, capable of changing by integral values only. The method will be illustrated by two examples.

I. In the quantum theory

$$S = k \lg \frac{(n+p-1)!}{(n-1)!p!}, \tag{1}$$

where n is the number of energy carriers and p the number of energy quanta, and the problem is to find the change in S produced by a change in p. Put

$$F=\lg\frac{(n+p-1)!}{(n-1)!p!} \tag{2}$$

Then
$$\Delta F=F(p+\Delta p)-F(p)$$
$$=\lg\frac{(n+p+\Delta p-1)!}{(p+\Delta p)!}-\lg\frac{(n+p-1)!}{p!}$$

since the term containing $\lg(n-1)!$ cancels. This may be written:

$$\Delta F=\lg\frac{(n+p+\Delta p-1)!p!}{(n+p-1)!(p+\Delta p)!}$$
$$=\lg\frac{(n+p)(n+p+1)\cdots(n+p+\Delta p-1)}{(p+1)(p+2)\cdots(p+\Delta p)}$$

If n and p are large numbers, and if Δp is a small integer, we have practically

$$\Delta F=\lg\frac{(n+p)^{\Delta p}}{(p+1)^{\Delta p}} \tag{3}$$

If Δp were unity, *i.e.*, if the change in p were made as small as it can be, this relation would be exact. If we now assume that for a large p the number $p+1$ may be replaced by p, we get

$$\frac{\Delta F}{\Delta p}=\lg\frac{n+p}{p} \tag{4}$$

The last expression leads directly to the quantized energy per carrier $\epsilon/(e^{\epsilon/kT}-1)$.

II. Another example is the well-known expression

$$S=k\lg\frac{n!}{(n_0)!(n_1)!\cdots(n_p)!} \tag{5}$$

The problem here is to find the maximum value of S, subject to the further restrictions that, because of the fixed number of energy carriers

$$n_0+n_1+\cdots=\sum n_i=n \tag{6}$$

and, because of the fixed energy of the system,

$$n_0(0\epsilon)+n_1(1\epsilon)+n_2(2\epsilon)+\cdots=\epsilon\sum in_i=E=p\epsilon \tag{7}$$

We put
$$G=\lg\frac{n!}{(n_0)!(n_1)!\cdots} \tag{8}$$

and
$$\Delta G=G(n_0+\Delta n_0,n_1+\Delta n_1,\cdots)-G(n_0,n_1,\cdots)$$
$$=\lg\frac{n_0!\quad n_1!\quad\cdots}{(n_0+\Delta n_0)!(n_1+\Delta n_1)!\cdots}$$

For a maximum value of G this should be zero. Hence

$$\Delta G = \lg \frac{1}{(n_0+1)(n_0+2)\cdots(n_0+\Delta n_0)\cdots(n_p+1)\cdots(n_p+\Delta n_p)} = 0$$

If the n_i are large integers and the Δn_i are small integers, this is very nearly

$$\Delta G = -\Delta n_0 \lg n_0 - \Delta n_1 \lg n_1 - \cdots \tag{9}$$

Hence the condition for a maximum is

$$\sum \Delta n_i \lg n_i = 0 \tag{10}$$

In addition to this we have from (6) and (7)

$$\sum \Delta n_i = 0 \tag{11}$$

$$\sum i \Delta n_i = 0 \tag{12}$$

The necessary and sufficient condition required to satisfy these last three equations is

$$a_1 \lg n_i + a_2 + a_3 i = a_4,$$

where a_1, a_2, a_3, and a_4 are constants. This yields

$$n_i = c_1 c_2^{\,i}, \tag{13}$$

where c_1 and c_2 are constants. These constants c_1 and c_2 may be evaluated in terms of the given constants E, p and n, and the energy distribution will be found to be according to Maxwell's distribution law. Since these further deductions present no new feature, they need not be considered here.

WORCESTER POLYTECHNIC INSTITUTE.
March 27, 1927.

BOOK REVIEWS

Die Seltenen Erden vom Standpunkte des Atombaues. GEORG v. HEVESY, Professor of Physical Chemistry in the University of Freiburg. Ever since the time of Mendelejeff, the rare earth elements have been considered the black sheep of the chemical family. Many attempts have been made to bring them into the fold of the periodic system, but all have been more ingenious than satisfactory. It remained for a physicist, Niels Bohr, to whom the author dedicates this monograph, to develop a scheme, based to some extent upon the earlier ideas of Thomson, which has been finally and completely successful. Another interesting example has thus been furnished of an event not uncommon in the history of science, where a problem frequently attacked without result receives its solution from a new and unexpected direction.

The wonderful advances that have been made possible by the application of Bohr's theory of atomic structure to this hitherto unpromising field are clearly and systematically described in the first half of the book (The Rare Earths and the Atomic Theory). Everything that was formerly chaos is now reduced to perfect order. Perhaps the one point which is not adequately explained is why a second series of rare earth elements does not begin with actinium, but so far as the first series is concerned the physicists have certainly cleared away all outstanding points of difficulty. On the chemical side, unfortunately, progress has not been equally rapid, and the descriptive sections which introduce the second half of the volume (The Chemical Properties and the Occurrence of the Rare Earths) suffer severely by contrast. The conclusion quoted at the top of p. 64 that the abnormally *small* increase in the equivalent conductivity of scandium sulfate with dilution is due to the extensive formation of inner complexes is obviously wrong, since the dissociation of such complexes with dilution necessarily involves an abnormally *large* increase in equivalent conductivity, as shown for example in the case of cadmium iodide. The concluding sections of the book, however, in which a brief return is made to physical topics (e.g., the effects of ionic size on isomorphism, etc.), rise to a very high level. The important work of Goldschmidt and his students on the occurrence and relative plentifulness of the rare earths is stressed in the last few pages, in the course of which one fact emerges which is rarely recognized, namely that the "rare earths" are not actually rare in nature. Not only do they occur openly in several fairly extensive deposits, but they are also existent in camouflaged form in many calcium and zirconium minerals. Their application to industrial uses evidently waits only for a more intensive study of their physical and chemical properties and for the development of more rapid and convenient methods of separation. To any research worker laboring along such lines, this admirable volume offers unique facilities and cannot be too highly recommended. Pp. 140+viii, 15 diagrams, Julius Springer, Berlin, 1927, 9 RM unbound; 10.20 RM bound.

JAMES KENDALL

Selenium, a List of References. MARION FOSTER DOTY. This list contains the titles of works relating to selenium, published between 1817 and 1925, owned by the New York Public Library. The book contains 114 pages, covering 1526 articles and a selected list of 138 patents. It is indexed as to authors, patentees, and subjects. The titles are classified in 14 groups. The list in each group is given in chronologic sequence. The more important divisions are the physical and chemical constants, the electrical and optical properties, the chemistry, and cells and their uses. The list is a very complete bibliography. Each reference gives the name of the author and a title. In many cases the title does not indicate clearly the scope of the subject. No attempt has been made to give a brief abstract in such cases. Also the titles of the foreign references are not translated into English. This is a defect for students not familiar with Italian, German, Russian, Swedish and French. But the compilation is very valuable in the location of the literature on selenium.—Pp. 114, The New York Public Library, 1927. 65 cents.

ROBERT J. PIERSOL

Catalysis in Theory and Practice. ERIC K. RIDEAL, Owen James Lecturer on Physical Chemistry, Cambridge University, England, and HUGH S. TAYLOR, Professor of Physical Chemistry, Princeton University. Second Edition.—The first edition of this work in 1919 gave the earliest systematic treatment of catalysis as an independent branch of physical chemistry. The seven years intervening between the first and the present edition have seen a rapidly increasing application of the principles of catalysis to practice. This extension has been "catalysed" in no small degree by this stimulating treatise from two of the foremost authorities in the field. The *theory* of catalysis, however, has lagged far behind its *practice*, in spite of the enormous efforts that have been put forth to gain an insight into its mechanism. This is especially true of contact catalysis to which the greater part of the work is devoted and in which most has been accomplished in practical application.

Two of the chapters new to the second edition are suggestive of the direction of much of the recent research, namely, those on "promoters" and on catalyst "poisons." The small amounts of the latter that have been found effective in greatly inhibiting catalytic reaction have given a clue to the small extent of the "active" surfaces. The study of the influence of different "promoters" has been of much practical value, but has added but few points of theoretical attack.

Anything approaching a complete theory enabling the prediction of those factors which have to be found out empirically seems far in the future. The authors have accordingly preferred to scatter the theoretical discussions throughout the text close to the illustrating material, rather than to attempt to segregate it into a self contained theory.

Catalysis in Organic and in Electro chemistry and by Radiant Energy are three of the most suggestive chapters, brought over from the first edition, to which much new material has been added. The authors are to be congratulated on their success in being able to cover a far greater amount of material without extensively enlarging the book. Pp. 516+xv, 31 figs. Macmillan and Company, London, 1926.

S. C. LIND

New Conceptions in Colloidal Chemistry. HERBERT FREUNDLICH.—This book may be regarded as a companion volume to, and supplementing the larger compendium, "Colloid and Capillary Chemistry" by Professor Freundlich, issued by the same publishers in the fall of 1926. The present volume covers the field of subject matter of the lectures which Professor Freundlich delivered at the University of Minnesota in the summer of 1925, although considerable new material in the way of references and comment has been added so as to bring the subject thoroughly up-to-date. As Freundlich points out, the recent developments in the theory and technique of colloid chemistry have necessitated certain modifications and extensions of our conceptions of colloidal behavior, and it is these considerations which are so beautifully set forth in the present volume.

It was the good fortune of the reviewer to be present when the lectures, upon which this book is based, were delivered, so that reading the present volume is like meeting an old friend who shows no traces of age but who has improved with the years. It is especially gratifying that now I am able to introduce this friend to many other persons who were unable to be present when the lectures were delivered. The volume contains eight chapters dealing respectively with Adsorption, The Electrokinetic Potential, Adsorption, Valency, and Coagulation, The Rate of Coagulation, The Stability of Hydrophilic Sols, The State of Aggregation and the Shape of Colloidal Particles, and Extent and Change of Surface in Colloidal Systems. Excellent subject and author indices are appended.

The book is not designed as an elementary text of colloid chemistry but rather to give a concise statement of certain very fundamental principles which, until recently, have been very generally ignored. The chapter on the electrokinetic potential is alone worth the price of the book. Colloid chemistry is rapidly passing from a qualitative to a quantitative science and the technique which this book suggests and illustrates should accelerate that change. Inasmuch as colloid chemistry borders so closely upon the domain of physics, this book should have an especial appeal to physicists. Pp. 142+vii, 47 figs. E. P. Dutton and Company, New York, 1927. $2.00.

ROSS AIKEN GORTNER

The Elements of Airfoil and Airscrew Theory. H. GLAUERT.—This is a clear and remarkably well written account of the modern applications of hydrodynamics to aeronautics. It contains an account of Joukowski's profile theory and the modifications and extensions introduced by von Mises and others. The Prandtl theory of induced drag and its applications to monoplanes and biplanes is delightfully presented. The application of Prandtl's methods to the interference of the wind tunnel is also given. One of the best chapters is the one on viscosity, which contains an account of the work of von Karman and others.

This is the best account of this phase of the subject that has yet appeared. The mathematics of the subject is given in sufficient detail but the physical significance is always admirably given. Pp. 228. Cambridge University Press, 1926.

C. L. E. MOORE

Practical Physics. T. G. BEDFORD.—This is a good example of the well-arranged, carefully written, rather conservative English text. Although intended primarily as a laboratory manual for first-year students, it omits some of the more rudimentary experiments, and includes a number that, particularly on the mathematical side, are decidedly beyond the average beginner. Most of the familiar experiments are found here, the laboratory instructions being preceded by development of the theory. In many cases the apparatus required is exceedingly simple, and illustrated with good diagrams. In a few places the lack of figure-references in the text is a source of annoyance. Many of the experiments, especially those on elasticity, reflect the influence of Searle. At the end of each chapter is given a list of further supplementary experiments. The section on light has to do mainly with geometrical optics, polarization being omitted. Considering the relatively advanced character of some of the experiments, the omission of the simpler experiments with alternating currents and of the measurement of self-inductance seems unfortunate, as well as the absence of reference to the three-electrode tube, which has now become a standard laboratory instrument. Nevertheless, the book should find favor with teachers of college physics on this side of the water.—Pp. 425+x, 225 figs. Longmans, Green & Co., Ltd., London, 1926. Price $3.50.

W. G. CADY

Problems of Modern Physics. H. A. LORENTZ. Edited by H. BATEMAN.—Every new development of atomic physics emphasizes the gulf existing between the classical electrodynamics with the group of phenomena which it describes so beautifully and the quantum theory together with those phenomena for the explanation of which its most extreme form seems to be absolutely demanded. How can interference of light ever be accounted for on any other than a wave theory? Yet the photoelectric effect, produced by the same radiation which exhibits interference over a distance of half a million wave lengths, is insistent in its demand for a corpuscular theory of light. In this book are collected the lectures presented by Professor Lorentz at the California Institute of Technology in 1922 together with extensive appendices in which are treated in more detail many topics which are only briefly discussed in the lectures. Beginning with the classical wave theory and electrodynamics, the author discusses critically the many points of conflict between the older point of view and that of the quantum theory and offers suggestions as to possible solutions of the dilemma.

The first major difficulty is that connected with the radiation from an accelerated electron demanded by Maxwell's equations. Does experiment reveal the existence of such radiation? Certainly the waves employed in wireless telegraphy are produced by rapidly alternating currents, and the experiments of Tolman and Stewart prove unequivocally that electric currents are due to the transport of electrons. Again the scattering of light by a gas as well as the scattering of x-rays seem to supply excellent evidence of the emission of radiation from accelerated electrons. On the other hand, how is the absence of radiation from the stationary states of the Bohr atom to be explained? The author rejects, on account of its teleological implications, the formal explanation founded on the assumption that the field of the electron is half retarded and half advanced. Instead he prefers to introduce electromotive forces of unknown origin sufficient to annul the radiation field. It is possible, however, that he is taking the Bohr model too literally. For a characteristic feature of the Bohr theory is the elimination of the dynamical frequencies in the final equations.

The second major point of divergence is that connected with the propagation of light. Can the wave theory demanded by interference and diffraction phenomena be reconciled with the corpuscular theory which is so successful in explaining the photoelectric effect and the Compton effect? The author discusses the suggestion made at various times by Slater, Einstein and Swann, and at one time rejected by Bohr, that the classical electromagnetic field carries no energy but acts merely as a guide for the propagation of energetic corpuscles. He finds much merit in this suggestion, but also certain difficulties.

The special relativity theory is discussed in some detail, and the book closes with an account of Einstein's theory of gravitation. Throughout, the text is notable for the author's lucid style and deep penetration. It is full of suggestions and should be an inspiration to the worker in research. The editor has added numerous notes and references which greatly enhance the value of the book. Pp. 312+vi. Ginn and Company, Boston, 1927. Price $3.60.

LEIGH PAGE